

# THE MODERN SOAP AND DETERGENT INDUSTRY

INCLUDING

## GLYCEROL MANUFACTURE

A Complete Practical Treatise in Three Volumes on the  
Manufacture of Laundry, Toilet, Pharmaceutical, Textile,  
Abrasive, Scouring, and Powdered Soaps ; also Detergent  
Compositions and Soap Substitutes of all kinds

Including Analyses of Raw Materials, Modern Patents and Literature, Recent  
Machinery and Processes, together with Numerous Practical Recipes, and  
Lay-out of Modern Soap Factories

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"SALT AND ALKALI INDUSTRY," ETC., ETC.

*IN THREE VOLUMES*

### VOL. III.—THE MANUFACTURE OF GLYCEROL

*(CONTAINING THE INDEX TO THE COMPLETE WORK)*



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# THE MODERN SOAP AND DETERGENT INDUSTRY

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## THE MANUFACTURE OF SPECIAL SOAPS AND DETERGENT COMPOSITIONS

TOILET SOAPS—SHAVING SOAPS AND CREAMS—TOOTH-CLEANING COMPOSITIONS—PHARMACEUTICAL, MEDICATED, AND DISINFECTING SOAPS—TEXTILE SOAPS OF ALL KINDS—CHIPPED AND FLAKED SOAPS—SOAP POWDERS—ABRASIVE AND POLISHING PREPARATIONS—SOFT SOAPS—HYDROCARBON AND PROTEIN SOAPS—SOAP SUBSTITUTES—LEATHER AND FURNITURE POLISHES—ALSO FULL METHODS OF ANALYSIS AND STATISTICS OF THE DETERGENT INDUSTRY.

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"The whole book is characterised throughout by the author's enthusiasm in the search for buried information and his determination to omit nothing which may prove of interest and value. The language throughout is concise and the elaborate system of sections and sub-sections renders the search for any particular information remarkably easy. We shall look forward to the third, and concluding, volume with interest. Dr Martin has certainly earned the gratitude of all those whose facilities for literary research are limited, but whose need for the results of it is great."—*The Chemical Age*.

". . . There is a mass of detail and incidental information in the book that is not indicated by the list of contents, but is quickly apparent on a perusal of the book.

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"No patented process of any consequence seems to have been omitted, and it may be a matter of some surprise to the reader to note the number and variety of these processes, many of which are obviously impractical, which have been the subjects of patents from time to time. . . .

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". . . Undoubtedly it will find a wide application as a convenient book of reference for those engaged in soap-making, although its maximum utility cannot be realised until Vol. III., with the complete index, is available."—*Chemical and Metallurgical Engineering* (New York).

"The work contains a great amount of information on the technology of detergents and their commercial forms."—*Journal of Franklin Institute*.

"A particular feature is the continual reference to recent patents, designed sometimes to effect what appear to be very slight improvements. These, indicating as they do attention to minute detail, will be carefully scanned by those engaged in the industry, since they apply to the mechanical rather than to the chemical side of the manufacture. One feature we regard as particularly valuable: the insistence on, or the approval given to, those processes in which the waste products are utilised. . . . Dr Martin takes a wide view of his subject and supplies much information on related topics."—*Engineering*.

LONDON: CROSBY LOCKWOOD & SON

# PREFACE TO VOLUME III

THIS volume on Glycerol completes the work on the Soap and Detergent Industry.

In it will be found practical details of modern plant and processes such as will be found in no other work published at the present time.

In addition to this, there has been given all the more important modern patents on Glycerol and a great many of the older ones, so that the reader can follow the lines of thought running through the minds of a long series of inventors, and possibly improve thereon.

For the same reason references are given to the original literature, as nothing is more instructive for the reader than to read through original papers. He thereby attains an insight into the difficulties of manufacture and a freshness of view which is impossible to impart in any short summary of the work.

The great advance made in the Glycerol industry within recent times will be obvious to anyone following these pages.

As in the two previous volumes dealing with Soap, an attempt is made to indicate fresh lines of progress in the Glycerol industry, and consequently full accounts are given of the remarkable new methods of fermenting sugars into Glycerol which developed in Germany, America, and France during the Great War.

Full accounts of the researches have been given, because they open up novel lines of thought which ultimately may revolutionise the whole subject and cause the invention of a whole series of new substances of great commercial importance.

It must be always remembered by the enterprising manufacturer that the scientific curiosities of to-day are the technical commonplaces of to-morrow. The history of every great technical success shows that it has been preceded by a long series of failures on somewhat similar lines. So that because a process is impracticable, or commercially unremunerative in the form it leaves the inventor, it by no means follows that it is useless to the technologist, because it may furnish him with new ideas which will lead to commercial success.

The mere fact that these new processes exist, and at the touch of a world famine sprang into vigorous life during the Great War, shows what possibilities still lurk unutilised awaiting the combined efforts of the research chemist and the commercial man.

Particulars are also given of the various "Glycerol substitutes" which have appeared on the market in recent times, as these are also "side-lines" which may become commercially important in the future.

The methods of analysis of Glycerol have been given very fully, so that the works chemist will have no difficulty in carrying out all the necessary estimations with the required degree of accuracy.

At the same time references are given to some of the more difficult and more unusual methods of analysis, so that the chemist, face to face with new problems of unexpected difficulty, will know where to turn for the necessary information.

Finally, a very complete Index has been compiled for the combined three volumes. It is hoped that this Index has been made as useful as possible by numerous cross references, so that the user, requiring the information on a particular subject, scattered in isolated statements over different volumes, will find them all under one head in the Index, and thus with little loss of time will be able to put his hands on the information required.

*Acknowledgments.*—The author wishes to acknowledge the help he has received in writing this work from many practical men employed in works.

As in war, so also in industry, many most valuable advances are made by men whose names never appear before the public and whose achievements are necessarily known only to a narrow circle. The industrial scientist stands here at a great disadvantage compared to his academic brother.

The help rendered the author by various firms has also been most valuable. In particular I must mention the names of Messrs Scott & Son Ltd., of London; Messrs Fullerton, Barclay, & Hodgart, of Paisley, Scotland; and Messrs Blair, Campbell, & M'Lean, of Govan, Glasgow; Messrs Manlove, Alliott, & Co., of Nottingham, England; Mr Reavel of the Kestner Evaporator Co. of London; last, but by no means least, Messrs Nobels Ltd., Ardeer, Scotland.

I have also to thank Messrs J. & A. Churchill Ltd., of London, for leave to use certain tables which appeared in Allan's "Commercial Analysis." Any author whose contributions have unwittingly been overlooked is asked to call the attention of the writer thereto, who would also be pleased to receive suggestions from practical men for increasing the utility of the work and for remedying any defects which necessarily must have crept into a large work of this nature; although every effort has been made to make the work as complete and as accurate as possible.

The labour of compilation has been very severe, and several years have been consumed in producing the complete work.



VOLUME III

THE MANUFACTURE OF GLYCEROL

INCLUDING

The Recovery from Soap Lyes, Distillation,  
Valuation, Analysis, Specifications, and the  
Manufacture of Polymerised Glycerols and  
Glycerol Substitutes



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## SECTION I

# The Manufacture of Crude Undistilled Glycerol





# CHAPTER I

## SOURCES OF GLYCEROL AND METHODS OF MANUFACTURE

### LITERATURE

- L. L. LAMBORN. "Modern Soaps, Candles, and Glycerine." Crosby Lockwood, London, 1906.
- WRIGHT-MITCHELL. "Oils, Fats, and Waxes." London, 1903.
- LEWKOWITSCH. "Oils, Fats, and Waxes." Vol. iii. London, 1909.
- S. W. KOPPE. "Glycerine." London, 1915.
- A. S. LANGMUIR. "The Twitchell Process and the Glycerine Trade," *Jour. Soc. Chem. Ind.*, 1917, 36, 180.
- THE TWITCHELL PROCESS, with a New Reagent. Joslin, Schmidt, & Co., Cincinnati, U.S.A.

### Glycerol Manufacture

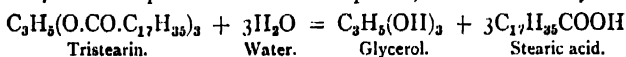
**Glycerol**<sup>1</sup> is mainly a by-product of the soap and stearin candle industries, although recently it has been obtained by the fermentation of sugars and similar substances. In practice it is obtained in dilute aqueous solution which contains many impurities, the exact nature and quantity of which depends upon the manufacturing process whereby it is produced.

For practical purposes the varieties of crude glycerol may be distinguished according to source, as follows :—

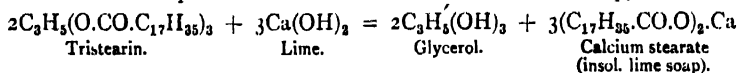
(1) **Soap Lye Glycerol, Soap Crude Glycerol.**—This represents the bulk of the glycerol prepared at the present time, and is obtained from the soap lyes remaining after the soap has been separated therefrom.

(2) **Crude Saponification Glycerol.**—This probably represents the purest of the crude commercial glycerols. It results from the saponification of fats by lime.

It will be recollected that (see the author's "Oils, Fats, and Waxes," p. 183) fatty acids are prepared for candle-making by saponification by lime. The fat is heated in an autoclave with water and lime to 176° C. at a pressure of 8-10 atmospheres, when the fat is hydrolysed thus :—



At the same time the lime present is turned into an insoluble calcium soap, thus :—



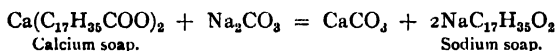
The glycerol water collects underneath the layer of liquid fatty acids and is finally drawn off; any calcium hydroxide in solution is neutralised by the addition of sulphuric acid, the liquid is filtered from the sludge of calcium sulphate, and evaporated.

---

<sup>1</sup> The pure chemical product is termed "glycerol" (which shows that it is an alcohol), while the impure commercial product is called "glycerine." Since this introduces an entirely superfluous complexity, we will throughout the article usually use only the scientifically correct term, viz., glycerol.

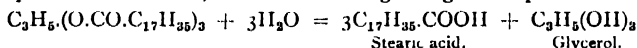
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Making soap by double decomposition of lime soaps with soda (see Vol. II., Section VI., p. 14, **Kreibitz's process**) also results in the production of a very pure crude glycerol. Here the calcium soap, obtained as above, is heated with sodium carbonate, thus :—



(3) **Crude Distillation Glycerol.**—This is the glycerol recovered from the acid waters resulting from the acid saponification process for making fatty acids.

It will be recollected (see the author's book, "Oils, Fats, and Waxes," p. 185) that the fats are heated with sulphuric acid in a still, when the following change takes place :—



The glycerol solution, containing free sulphuric acid, collects beneath the layer of fatty acid and is run off, and the sulphuric acid neutralised by lime.

The glycerol obtained from this source goes by the name "crude distillation glycerol," because the fatty acids obtained by this process must be distilled to yield a good candle-making material.

(4) **Twitchell's Crude Glycerol.**—This is obtained by working up the acid waters resulting from Twitchell's saponification process (see the author's "Oils, Fats, and Waxes," p. 186).

(5) **The Connstein Fermentation Crude Glycerol.**—This is glycerol obtained by splitting the fats by means of a ferment.

(6) **Glycerol Obtained by Fermenting Sugar.**—The preparation of glycerol by the fermentation of sugar is of modern origin, having been developed in Germany during the war. The process will be treated separately in Chapter I., Section III., below.

### Advantages and Disadvantages of the Various Crude Glycerols

It will be recollected that the prevailing method for the manufacture of soap consists in the saponification of the fat by boiling with caustic soda lye. The fatty acids combine with soda as soap, which is separated by the addition of salt, and comes to the surface in the molten condition. The glycerine is set free and remains dissolved in the spent lye. It is contaminated by the presence of the salt used to render the soap insoluble. During the concentration of the spent lye for the recovery of the glycerol a large quantity of salt is thrown out, making the evaporation somewhat difficult, although this difficulty has been largely eliminated of late years by the use of properly designed evaporators working *in vacuo*. The final crude glycerol is a saturated solution of sodium chloride and some sulphate together with sodium salts of the lower fatty acids, in glycerine and water. The glycerol averages about 80 per cent. and contains about 10 per cent. mineral salts.

The glycerine refiner distils this crude soap lye glycerine with superheated steam *in vacuo* for the production of dynamite glycerine and chemically pure glycerol. The presence of so much salt raises the boiling point of the glycerine and reduces its vapour tension so that the output is reduced. Furthermore, the salt accumulates in the still, producing, finally, a semi-solid mass of salt and glycerol, together with tarry matters which constitute the "foots" of the glycerine trade. It is a difficult matter to extract all the glycerol from this residue without undue loss. The treatment of the "foots" is one of the problems of the glycerine trade.

The recovery of glycerol, separated from fats by "splitting" them by means of **Twitchell's reagent**, by the lime saponification process (**Kreibitz's**

process, etc.), or the **Connstein ferment process**, is obviously much more simple than the recovery of glycerol from soap lyes, because there is a much smaller amount of inorganic salts to be removed in the latter cases; also the "foots" left when the glycerol is distilled is less; consequently the glycerol is cheaper and simpler to prepare in a pure state by these latter processes, and the glycerol distiller, therefore, prefers a crude glycerol which is free from this large admixture of salt.

Up to 1889, indeed, chemically pure or dynamite glycerol was obtained entirely from the crude glycerol of the candle-makers, known as **saponification** or **candle crude**. It was the by-product of the candle factory, and was produced by the breaking up of fat in autoclaves by heating under pressures of 200 lbs. and more with water and a little lime. The fat was split into fatty acids and glycerine directly, and the latter was a product of considerable purity, containing about 88 per cent. glycerine and less than 1 per cent. of mineral matter.

No satisfactory plant existed at that time for recovering the pure glycerol from soap lyes, consequently the latter, in former days, were simply run down the drains as waste liquor, whereas at the present time the yield of glycerol from soap lyes is one of the main sources of profit of cheap soaps. The cause of this great change was the greatly increased demand for glycerine for explosives. The soap-makers now found it profitable to work them up; to-day, scarcely a soap plant can be found that does not recover its glycerine as a by-product. Indeed, by means of modern processes of refining (described below) the glycerol from this source can be obtained of excellent quality (*i.e.*, as regards organic impurities), provided that good class oils and fats have been used for soap-making. This change in the business compelled refiners to develop methods for distilling soap lye crude glycerine, and eventually the larger refiners were working mainly on soap lye rather than candle crude, although there were still a number of glycerine refiners who worked exclusively on candle crudes. Saponification crudes free from salt have always been in greater demand, and have commanded a higher price per unit of glycerine. For several years before the advent of the **Twitchell process** it looked as if saponification glycerines would practically disappear as a raw material in glycerine refining, but with the success of this process the Twitchell saponification crudes made their appearance and are now factors of very considerable importance.

The ideal of the glycerine refiner has thus been the production of a saponification rather than a soap lye crude by the soap manufacturer. It has also been the hope of the soap trade to obtain directly by the deglycerising of the fat a relatively pure glycerine as a by-product and free fatty acids which could be combined with the cheap alkali, sodium carbonate, to make soap instead of the relatively expensive caustic soda. To meet this need have been developed the **Twitchell process**, the **Kreibitz** lime saponification method, and the **Connstein** process.

It must be remembered, however, that the soap maker cannot in most cases adopt the latter processes, as it would mean a complete alteration in the brands and quality of his soaps, the best quality soap being still made by the "boiled process," although on the Continent the processes of making soaps direct from fatty acids is growing in favour, because the public there are not quite so exacting as regards the appearance and quality of the soap they demand.

Hence it is probable that for many years yet glycerol will continue to be made from soap lyes in this country.

**The Twitchell process** is characterised by its simplicity and the low cost of the plant. Prior to Twitchell's discovery, free fatty acids could only be obtained by the autoclave process, involving a heavy capital outlay for copper apparatus, which could only be used in small units and at a high temperature and pressure, making the operation expensive and somewhat dangerous. The autoclave

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saponification was used only in the preparation of fatty acids for candle manufacture, as the process was too costly to be used in the production of fatty acids to be used in soaps. The Twitchell process is effected in loosely closed wooden tanks by digestion with water and as little as 0.5 per cent. of the reagent, and at a temperature not exceeding that of exhaust steam. The reaction may be carried out on a scale limited only by the size of the tank. The Twitchell process has made possible the saponification of fats on a huge scale for the direct production of free fatty acids for the improvement of their purity and colour. It has opened up for the soap trade the use of low grade fats, such as garbage grease and cottonseed oil foots, the distilled fatty acids being combined directly with carbonate of soda to produce light coloured soaps, and the glycerine being made available for the manufacture of dynamite glycerine. In this way the Twitchell process has benefited the glycerine trade by opening up new sources of supply which were previously unavailable.

There is no evidence that Twitchell crude glycerol is any less pure than the saponification glycerine prepared by other processes, providing the fat used as a raw material is reasonably pure. Of course, a crude glycerine manufactured from a low grade fat will fall behind a crude made from good tallow, but this is the fault of the fat and not of the Twitchell process.

Dr Twitchell claims the following advantages for his process :—

(1) Ninety-five per cent. of all the glycerol in the fat can be obtained as "dynamite" glycerol, or chemically pure. This gives yields as follows :—

Good tallow	-	-	-	-	9.5 to 10	per cent. absolute glycerol.
Coco-nut oil	-	-	-	-	13 to 13.5	" " "
Cotton oil	-	-	-	-	10	" " "
Grease and poor tallow	-	-	-	-	6 to 8	" " "

(2) The glycerol water to be evaporated is 15 per cent. concentrated instead of 3.4 per cent. as in spent soap lye, and hence but one *quarter* as much water has to be removed in evaporating to crude glycerol as is the case with waste soap lyes. In addition, as the glycerol water contains no salt, the water which has to be evaporated is much more easily removed, with a consequent reduction of the loss of glycerol to almost nothing, and the production of a crude glycerol containing 90 per cent. *absolute glycerol* with much greater ease and less expense than an 80 per cent. crude can be produced from waste soap lyes.

(3) The crude glycerol obtained is of the quality of best candle crude, contains but a few tenths of 1 per cent. of ash, and is much superior to that obtained from soap lye.

(4) Dynamite or chemically pure glycerol can be made in one distillation.

(5) A glycerol still will handle 50 per cent. more per hour of this crude than of soap lye crude, and produce a refined glycerol of better quality with less foots.

(6) The fatty acids are of better odour than the original stock.

(7) The fatty acids can be saponified with soda ash instead of caustic soda.

(8) As the saponifier used to bring about this separation yields about three-quarters of its weight of fatty acid, the real cost of recovering glycerol is reduced by this amount.

(9) Soap powder can be made directly from the fatty acids in the crutcher, or mixed with soda ash without using the crutcher at all.

(10) The glycerine is separated from the fat in covered wooden tanks with exhaust or live steam at low pressure ; requires no expensive boiler plants, building, or skilled labour.

The *Kreibitz* process also produces extremely pure and concentrated glycerol, but requires enormous quantities of lime, and the disposal of the resulting calcium carbonate sludge is a source of trouble and expense.

In the chapters below, the most convenient method of procedure will be to describe the process of manufacturing glycerol by each of these processes in order, dealing first with the manufacture of glycerol from soap lyes.

# GLYCEROL AND METHODS OF MANUFACTURE

## Sources and Yield of Glycerol

The following represents the yields of glycerol obtainable practically from different materials used for soap-making :—

100 parts of tallow	give	9 parts of 80 per cent. glycerol.
" cotton-seed oil	" 10	" " "
" coco-nut oil	" 12	" " "
" palm-kernel oil	" 13	" " "
" olive oil	" 10	" " "
" palm oil	" 6	" " "
" greases (bone fats)	" 6.8	" " "

The materials vary in glycerol content with the methods of preparation ; especially is this the case with tallows and greases.

Every care should be taken that the raw materials are fresh, and they should be carefully examined to ascertain if any decomposition has taken place in the glycerides. This would be denoted by the presence of an excess of free acidity, and the amount of glycerol obtainable from such a fat would be correspondingly reduced.

The following table is supplied by Dr Twitchell, as representing the yield of glycerol from various materials when the glycerol is obtained by his process :—

TABLE SHOWING GLYCEROL AND FATTY ACID CONTENTS OF VARIOUS FATS AND OILS

Name of Oil or Fat	Pure Glycerol Content of Absolutely Neutral Oil.	Total Fatty Acid Content.	Average Content of Free Fatty Acid in Commercial Oil.	Pure Glycerol Content of Commercial Oil.	Yield of Pure Glycerol, 28° Bé., in Commercial Oil.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Cotton-seed oil - -	10.6	95.96	Trace	10.6	12.05
Peanut oil - - -	10.4	95.8	5.20	8.3-9.9	9.43-11.25
Flaxseed oil - - -	10.4	95	1.2	10.3-10.4	11.70-11.82
Coco-nut oil - - -	13.9	94-94.6	3.5	13.2-13.5	15-15.34
Coco-nut oil (off) - -	...	94-94.8	15.40	8.3-11.8	9.43-13.41
Bone grease - - -	10.5	95	20.50	5.2-8.4	5.91-9.55
Linseed oil - - -	10.5	95.5	1.2	10.4-10.5	11.82-11.93
Corn oil - - -	10.4	94-96	1.10	9.3-10.3	10.57-11.70
Olive oil - - -	10.3	95	2.25	7.7-10.2	8.75-11.59
Palm-kernel oil - - -	13.3	94-94.6	4.8	12.2-12.8	13.87-14.55
Palm oil - - -	11.0	95	10.50	5.5-10.0	6.25-11.37
Horse grease - - -	10.6	95-96	1.3	10.5-10.6	11.93-12.05
Castor oil - - -	9.8	94.5-95	0.5-10	8.8-9.8	10-11.14
Beef tallow - - -	10.7	95.6	5	10.2	11.59
Rapeseed oil - - -	9.7	95	1.7	9.9.7	10.23-11.02
Sesame oil - - -	10.3	95.5	5.15	8.7-9.8	9.89-11.14
Soya bean oil - - -	10.4	95.5	2	10.2	11.59
Sunflower seed oil - -	10.4	95	1.5	9.9-10.3	11.25-11.70
Sulphur oils (extracted from olive press cake)	...	95	30-60	4.7	4.55-7.95
Hog's grease - - -	10.6	94-96	0.5-1	10.5-10.6	11.93-12.05
Vegetable tallow - - -	10.9	94-95	1.3	10.5-10.8	11.93-12.28
Blubber oils - - -	10.0	94-95.5	2.20	8-9.8	9.09-11.14
Train - - -	10.0	94-95.5	2.20	8-9.8	9.09-11.14

# CHAPTER II

## OUTLINES OF PROCESS OF OBTAINING GLYCEROL FROM WASTE SOAP LYES

THE recovery of **glycerol from soap lyes** is complicated by the fact that the solution contains dissolved soap, albuminous matter, salt (used for salting out the soap), a little sodium carbonate, and a small amount of caustic soda and

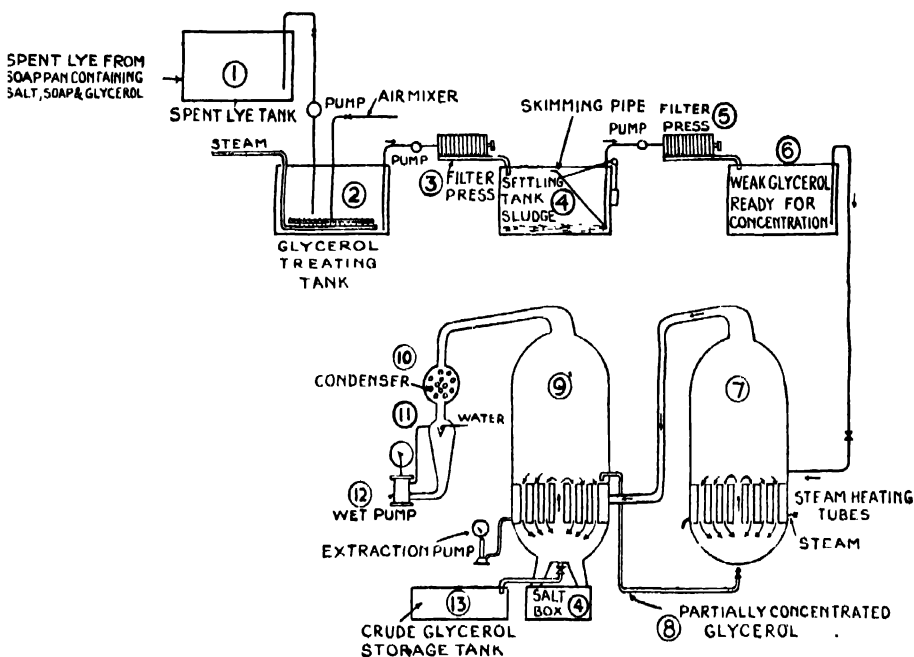


FIG. 1. —Flow Sheet for Manufacture of Glycerol from Soap Lyes.

sodium salts of organic acids. Hence these impurities must be removed, the soap being eliminated by precipitation with alum or other chemicals, while the salt can only be commercially removed by evaporating the solution and allowing the salt to crystallise out.

Moreover, the crude glycerol thus separated from the crystals will still contain a considerable amount of sodium salts of organic acids and salt, and consequently these are left behind when the glycerol is distilled in the form of troublesome "glycerine foots." Consequently the recovery of glycerol from soap lyes is a complicated and difficult process, which, however, has long been successfully carried out by means of modern plant.

The simplest method of procedure is to first describe the general outline of

procedure and then give details of the plant and processes recommended by the different makers and authors.

Fig. 1 represents a flow sheet for the manufacture of glycerol from soap lyes. The spent lye from the soap pan is run into tank 1 and allowed to settle, so that soap separates at the top and impurities at the bottom. The lye is pumped off into the glycerol treating tank 2. Here it is treated with chemicals (such as alum, barium, chloride, etc.) which precipitate any soap present, also albuminous matters and impurities.

This tank is usually provided with a live steam heating coil and also an air agitator. After well agitating and heating, the liquor is pumped through the filter press 3 (which retains the precipitated sludge) into a settling tank 4, where it is allowed to settle. The clear liquid is then pumped from 4 through the filter press 5, and is then sufficiently purified for evaporation. In small works the extra filter press 5 may be dispensed with, the liquor from tank 4 being pumped back through the filter press 3 and thence into the tank 6.

From 6 it is sucked by the vacuum into a vacuum evaporator 7, where the liquor is partially concentrated by heat supplied by steam-heating tubes. The partially concentrated liquor flows through the tube 8 into the second vacuum

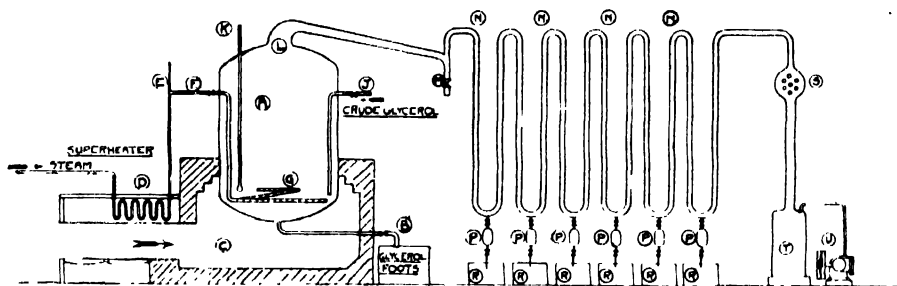


FIG. 2.—Glycerol Distillation Plant.

evaporator 9, where it is further evaporated, the heat being supplied by the hot vapours from the first evaporator 7, passing to the heating tubes in 9 as shown. The hot vapours from 9 are condensed by cooling water circulating in the condenser 10, the process being completed by a jet condenser 11, worked by the wet pump, which also creates the vacuum in 9.

As the result of this concentration the salt separates out from the liquor in 9 and is removed, as described below, by means of the salt box 12. The concentrated crude glycerol passes from 9 into the storage tank 13.

**Distilling the Glycerol.**—The crude glycerol must now be distilled, clarified, and concentrated. Fig. 2 shows a diagrammatic view of the plant usually employed. In modern practice the distillation is always effected under vacuum, as a saving of over 25 per cent. in cost is thereby effected as compared with the old process of distilling under ordinary atmospheric pressure. The crude glycerol passes from the storage tank by means of the pipe j into the still A (being sucked in by means of the vacuum). This still may be made of cast iron, wrought iron, or copper. At the bottom is a run-off pipe B to allow the residual "foots" to be removed after the operation of distillation is completed. In modern plant the still is usually heated by superheated steam obtained from the power plant after expansion. In older plant the still is heated by a coke fire (or by gas firing) as indicated, the hot furnace gas serving also to superheat the steam in the superheater D, the amount of superheat being regulated by dampers (not shown). The temperature of the entering superheated steam is indicated by the thermometer E.

The superheated steam passes directly into the glycerol by means of the perforated coil G. The temperature prevailing within the still is indicated by a thermometer K.

Under the vacuum prevailing, the mixture of glycerol vapours and steam passes through L into a series of air-condensing pipes NNN, the various fractions of glycerol condensing in them being removable separately from each set by means of the drums PPP. The final condensation of steam may be effected by water

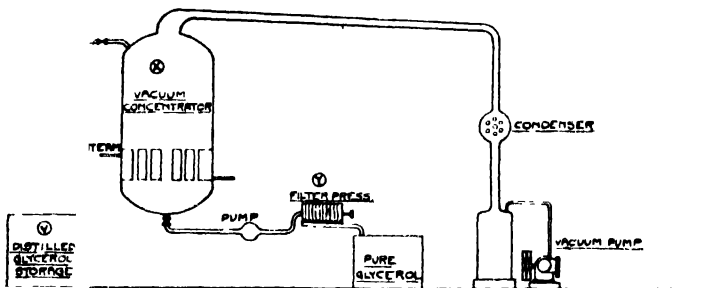


FIG. 3.—Concentrating and Clarification of the Distilled Glycerol.

cooling in the condenser S—often in conjunction with a wet jet condenser. U is the vacuum pump.

**Decolorising the Glycerol.**—The distilled glycerol must now be clarified and concentrated (since it contains some water from the steam). In the plate shown in Fig. 3 the distilled glycerol is therefore mixed in a tank V with the correct amount of decolorising charcoal, concentrated in the vacuum evaporator X to the correct concentration, and the charcoal removed by forcing the product through the filter press Y.

Many works prefer to heat the glycerol with charcoal in a separate vessel, to 80°-100° C., then force the mass through the filter press into the concentrator and evaporate under vacuum to the desired consistency.



## CHAPTER III

SOAP LYE GLYCEROL (*continued*).—PROCESSES  
FOR TREATING THE SOAP LYE  
PREVIOUS TO CONCENTRATION FOR  
SALT RECOVERY

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BEFORE concentrating the lye in order to separate the salt by crystallisation it is necessary to treat the lye chemically in order to remove various organic and inorganic impurities present.

The lye, as discharged from the soap pan, contains in addition to the glycerol some dissolved soap, albuminous matter, salts of organic acids, salt used for graining the soap, and small amounts of free caustic soda, sodium carbonate, etc. Hence the principle involved in the purification is to add free *mineral acid* to decompose the soap and set free the fatty acids, and then add to the solution a metallic salt such as alum, which will precipitate the fatty acids as aluminium soaps and albuminous matter, leaving the salt in solution.

Before describing the various processes which have been proposed for this purpose, a few words will be necessary on the constitution of ordinary soap lyes.

The waste lye as discharged from the soap kettle should contain 4-8 per cent. of glycerol, and be nearly neutral (0.0-0.2 per cent. NaOH are limits of alkalimetry), otherwise much valuable acid will be wasted in neutralising the excess of alkali.

The specific gravity of the spent lyes varies, as a rule, from 1.08-1.14, according to the quantity of dissolved salt (8-14 per cent.).

M'Bain and Walls (*loc. cit.* above) give the approximate composition of the spent lyes (stock lye) of a well-run soap works, like the Broad Plain Soap Works of Bristol, as follows :—

First Lye.	Per Cent.
NaOH - - - - -	0.0-0.15
Na <sub>2</sub> CO <sub>3</sub> - - - - -	0.5-0.99
NaCl - - - - -	8.0-18
Glycerol - - - - -	4.0-5.5
Sp. gr. - - - - -	1.09

The greater the inferiority of the stock used in the manufacture of soap, the greater will be the cost of recovery of the glycerol present in the lye, both on account of the great amount of foreign organic matter present in the lye, which must be removed, and also because of the smaller amount of glycerol present in the stock.

Formerly, when impure caustic soda—*e.g.*, black ash—was used, the resulting crude glycerol contained such impurities as sodium sulphate, sodium sulphite, sodium thiosulphate, and sodium thiocyanate, and this made the glycerol difficult to purify. At the present time very pure alkalis are usually used, and the presence of sulphides and sulphites in the glycerol is usually avoided. The presence of arsenic in the chemicals to be used must be looked for by the analyst, as once this poison is introduced into the glycerol it is very difficult to eliminate it (see Section IV., p. 11).

According to Lewis, it is impossible to eliminate arsenic to below 2 parts per million, except electrolytically.

However, commercial HCl is now obtainable of arsenic content not more than 5 parts per 10,000,000.

As the value of the lye depends upon the percentage of glycerol therein and on its comparative freedom from free caustic alkali, sodium carbonate, and organic impurities, the works chemist should rapidly estimate these quantities previous to purification.

The methods used for analysis are explained below, Section VI., on "Analyses of Glycerol."

The first lye drawn from the soap pan or kettle contains the highest percentage of glycerol, but according to Sanger (*Chem. and Metall. Chem. Eng.*, vol. xxvi., No. 26, June 28, 1922), as many as thirty succeeding draw-offs will show glycerine on analysis.

The following table shows this :—

(30,000 lbs. of tallow containing 85.3 per cent. of neutral fat were saponified in the soap pan and the excessive lyes withdrawn.)

	Weight. Lbs.	Glycerol. Per Cent.
(1) Killing change - - - - -	12,742	8.47
(2) Rosin change - - - - -	7,202	4.65
(3) First wash - - - - -	5,263	3.76
(4) Second wash - - - - -	3,787	3.30
(5) Third wash - - - - -	8,033	2.80
(6) Fourth wash - - - - -	7,202	2.36
(7) Fifth wash - - - - -	7,479	2.10
(8) Sixth wash - - - - -	8,033	1.96

Obviously the amount of lye to be drawn from a kettle will depend on the price one can obtain for the glycerol.

When the lyes show too low a percentage of glycerol the cost of evaporation, etc., will exceed the value of the glycerol obtained.

According to M'Bain and Walls, from experiments conducted at the *Broad Plain Soap Works* at Bristol, the soap at the first "salting out," "graining," or "relargage" contains about 0.5 per cent. glycerol of the original 10 per cent. of glycerol combined in the fat.

On regaining this soap ("third change," "washing") with salt the separated lye (which contains most of the remaining glycerol) is pumped off. This process of regaining may be repeated, and finally the soap is "*boiled on strength*" (fourth change, strengthening change, clear

boiling, coction) by adding successively small quantities of *alkali* (32° Tw., 1.162 sp. gr., 14.35 per cent. NaOH, 3.6 *normal*) until about 2 per cent. of the weight of the soap (reckoning the alkali as Na<sub>2</sub>O) has been added and the whole boiled with clear steam for two hours or more.

The object of "*boiling on strength*" is to ensure complete saponification since there may be as much as 20 per cent. unsaponified fat left at the end of the first change. The "*half-spent*" (strength lye) which settle out are strongly alkaline and have the following approximate composition :—

**Approximate Composition of Half-Spent Lyes (Strength Lyes)**

	Per Cent.
NaOH	5.6
Na <sub>2</sub> CO <sub>3</sub>	1.2
Glycerol	3
NaCl	4.6
	<hr/>
	13.14

**Lye Storage Tanks.**—It is obvious that there must be enough tank storage capacity to hold the spent lye produced during any one week. The lyes are thus enabled to cool sufficiently to separate the soap before passing on for glycerol recovery.

Lyes must not be allowed to stand too long owing to bacterial activity injuring the quality of the glycerol.

**Specification for Soap Crude Glycerine.**—The lye as it comes from the soap pans can, without chemical treatment, be concentrated until it contains as much as 40 per cent. glycerol.

In this form, however, it contains so much ash and impurity as to be practically unsaleable to the glycerol refiners. To give it a market value the impurities must be removed and the liquid concentrated until it conforms to the following specification :—

Analysis to be made in accordance with the International Standard Methods (I.M.S., 1911) described below.

**Glycerol.**—The standard shall be 80 per cent. glycerol. Any crude glycerine tendered which tests 81 per cent. glycerol or over shall be paid for at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerine tendered which tests under 80 per cent., but is 78 per cent. or over, shall be subject to a reduction of one and one-half times the shortage calculated at *pro rata* price as from 80 per cent. If the test falls below 78 per cent., the buyer shall have the right of rejection.

**Ash.**—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10.5 per cent., a percentage deduction shall be made for the price for the excess calculated as from 10 per cent. at contract price, and if the percentage of ash exceeds 10.5 per cent., an additional percentage reduction shall be made equal to double the amount in excess of 10.5 per cent. If the amount of ash exceeds 11 per cent., the buyer shall have the right to reject the parcel.

**Organic Residue.**—The standard shall be 3 per cent. A percentage deduction shall be made of three times the amount in excess of the standard of 3 per cent. calculated at contract price. The buyer shall have the right to reject any parcel which tests over 3.75 per cent.

### Processes for Treating the Lye

There are many processes for treating the soap lye so as to make it conform to the preceding specification, which we will now describe :—

(1) **Iron Alum Process of Purification.**—The waste lye reduced to its lowest practicable degree of alkalimetry, viz., 0.3-0.4 per cent. NaOH and Na<sub>2</sub>CO<sub>3</sub>, is run from the soap kettle to the storage tanks to cool. Here any dissolved soap separates on the surface and is skimmed off, while heavy impurities sink to the bottom. The liquor is then run into the treating tank A (Fig. 4), made of sheet steel and provided with open steam pipes at the bottom for heating, and an air jet for mechanical agitation. The treatment tank is filled to about 24 in. from the top so as to allow space for agitation, and a steam blower or ejector is turned on for the double purpose of stirring the lye with air, and at the same

time heating it. After a few minutes of agitation a sample is withdrawn before any metallic salt or acid is added, and tested. If the waste lye is strongly alkaline, either sulphuric or hydrochloric acid is now run in until the liquor is almost neutral, and then basic ferric sulphate solution added in the proper proportions (usually about 0.5 per cent. is sufficient). If, however, the liquid is only slightly alkaline, the iron salt alone is used for neutralisation. Usually three-fourths of the alkali are neutralised by acid and the remainder by the basic iron sulphate.

The iron salt is known as "chemical sand," and is made by mixing a finely powdered and dried iron ore (analysing 50 per cent. iron oxide) with concentrated sulphuric acid (60° Bé) previously heated to 150° C. The mass is then run on to an iron floor, where the reaction continues and the mass solidifies. It is then broken up and heated for some hours at 200°-280° C. It then forms a mixture of ferric sulphate, ferric oxide, and a little free acid. Instead of this iron salt any of the alums may be used as a precipitant. They are, however, somewhat more expensive.

Sometimes *ferric chloride*,  $FeCl_3$ , is used as the precipitating agent. It is made by dissolving ferric oxide in hydrochloric acid (muriatic acid, 20°).

The acid added to the soap lye decomposes any soap present, setting free the fatty acids.

The iron salt then precipitates these acids as insoluble iron soaps, and at the same time carries down any albuminous matter (coagulated by heat).

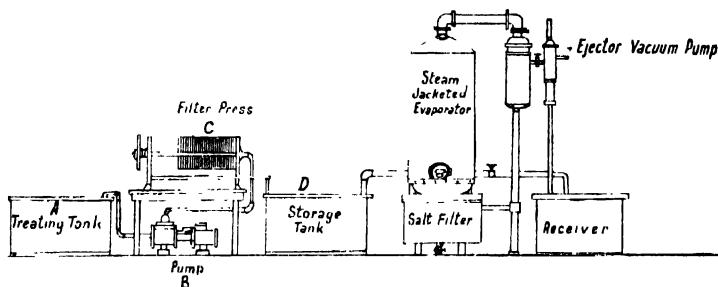


FIG. 4.—Iron Alum Process of Glycerol Recovery from Soap Lye.

The lyes are agitated with air while the chemicals are being added. The lye is then forced by means of the pump *B* through the filter press *C*, which retains the precipitated impurities, the lye flowing into another similar tank (not shown) where the process of purification is completed. The lye is then filtered off into the third tank *D*. It should now be clear, and possess a slight acid reaction. The exact amount of dry soda ash to neutralise the liquor is now thrown in and thoroughly mixed, and the lye filtered from the resulting precipitate. The lye is now drawn off into the vacuum evaporator and concentrated, as described in the next chapter, until it contains 80-85 per cent. glycerol, 6-8 per cent. salt, and possesses a specific gravity of 34° Bé.

(2) **Aluminium Sulphate Process (Double Treatment).**—The soap lyes are placed in a lead-lined tank, and commercial hydrochloric acid is slowly run in until a piece of blue litmus paper is just slightly reddened by the lye. Then ordinary alum solution is added until all the free fatty acids present are precipitated as aluminium soaps. From 3.5 lbs. of sulphate of alumina per 1,000 lbs. of lye treated is added, the exact amount being determined by experience, and will vary with the nature of soap made and plant practice. The liquor is now agitated with air until a sample taken from the tank, and filtered, gives a clear filtrate. When this occurs the contents of the tank is passed through the filter press as previously described. The scum which accumulates on the treatment tank is usually transferred to a perforated box suspended over the tank, and the liquor allowed to drain from it.

The liquor is now made just alkaline by adding caustic soda or sodium carbonate, and is once again filtered.

The filtered liquor is now ready for evaporation and distillation.

W. E. Sanger recommends the following process as prevalent in the United States :—

The settled, cooled, and skimmed lye is pumped to the treatment tank.

Sulphate of alumina is then added to the first treatment tank in amount determined by experience.

The liquid is well stirred, warmed, and sulphuric acid (60° Bé.) is slowly run into the tank so that the acid is neutralised almost as soon as it enters the tank.

As soon as there has been added enough acid to turn blue litmus red, the charge is agitated for several minutes to ensure mixing, and is finally tested with litmus, which it must turn red.

The lye is then filtered into a second treatment tank where caustic soda of any desired strength is added until a sample will just turn red litmus blue.

A filtered sample of the lye is tested with a few drops of a 10 per cent. solution of sulphate of alumina.

If a turbidity results, more aluminium sulphate is added to the second treatment tank to complete the precipitation of anything that can be precipitated by this salt.

The lye is then filtered and is ready for evaporation.

One precaution must be observed. The caustic-treated lye must never be filtered through a press which has in it any filter press cake belonging to an acid filtration, as this would dissolve some of the precipitate obtained in the acid treatment.

### **Lye Purification by Single Treatment with Aluminium Sulphate.—**

This is widely used, but of course is probably not quite so efficient as the preceding methods. It is, however, simple. The lye is merely treated with aluminium sulphate.

The cooled and settled lye, from which the soap has been removed, is pumped into a tank as before, agitated with air, and steam heated as before.

Next a sample is withdrawn, from 3-5 lbs. of sulphate of alumina is added to the tank for each 1,000 lbs. of spent lye, the exact amount being determined by experience and the nature of the stock used.

**Chemical Control of Single Treatment Process.**—The following details are typical of the chemical control carried out by the works chemist during the preceding operation.

For simplicity of discussion, assume that sulphate of alumina and 60° sulphuric acid is used.

Assume that a sample has been withdrawn from the treatment tank *before* adding the aluminium sulphate.

This sample is filtered and tested.

It is most convenient to make the test on 10 c.c. samples, using N/4 NaOH and N/4 H<sub>2</sub>SO<sub>4</sub>, since 1 c.c. of standard solution is then equivalent to practically 0.1 per cent. of acid or alkali (respectively) in the sample. Phenolphthalein is used as indicator, 1 g. being dissolved in 50 c.c. of alcohol and neutralised with caustic soda to form the stock solution.

We shall assume that the treatment tank is 8 ft. inside diameter and 8 ft. deep inside, and that it is filled to a depth of 70 in. with spent lye. A tank of this diameter holds 261.4 lbs. of water per inch of depth, so that 70 in. would weigh 18,298 lbs. Spent lye is somewhat heavier than water, but calculations are made on water weights to avoid using an excess of materials and so that errors will be made on the correct side.

After adding three or four drops of indicator to a 10 c.c. sample of the filtered fresh lye, N/4 acid is run in from a burette until the pink colour has been discharged and then an excess of about 4 c.c. is added to neutralise any carbonates or bicarbonates which may be present. Let us assume that the total amount of N/4 acid added is 7.2 c.c. After boiling vigorously to expel carbon dioxide, the solution is cooled and the excess acid is titrated with the N/4 NaOH until the sample remains pink on standing a short time. Assuming that 2.5 c.c. was required, the difference between 7.2 and 2.5, or 4.7 c.c., is the amount of N/4 acid necessary to neutralise

the alkali in the sample, or since each c.c. of N/4 acid is equivalent to 0.1 per cent. of alkali, the original spent lye contained 0.47 per cent. of alkali.

In the treatment tank there is 18,298 lbs. of spent lye testing 0.47 per cent. alkaline or containing 0.47 per cent. of NaOH; 18,298 times 0.0047 equals 86 lbs. of NaOH which must be neutralised.

Assume that the lye under consideration required 3 lbs. of sulphate of alumina for each 1,000 lbs. of spent lye and that this salt was added *after* the first sample was taken.

Accordingly, 48 lbs. of sulphate of alumina was added to the treatment tank after the first sample was taken.

This salt neutralises about one-third of its weight of NaOH, therefore about 16 lbs. of NaOH has been neutralised, leaving 70 lbs. still to be neutralised. Since 1.57 lb. of 60° sulphuric acid will neutralise 1 lb. of NaOH,  $70 \times 1.57$ , or 110 lbs., of 60°  $\text{H}_2\text{SO}_4$  is added to the treatment tank, and the charge is thoroughly agitated for about five minutes.

A second sample is then taken, filtered, and 10 c.c. tested exactly as before. Assume 4.2 c.c. N/4  $\text{H}_2\text{SO}_4$  added and 3.6 c.c. N/4 NaOH required to titrate back. The lye is still slightly alkaline—0.06 per cent.—and since the original charge of 18,298 lbs. has been increased by 95 lbs.,  $18,393 \times 0.0006$ , or 11 lbs., of NaOH still remains to be neutralised, requiring 17 lbs. of 60°  $\text{H}_2\text{SO}_4$ . This is added, the mixture thoroughly agitated for a few minutes and another sample taken, filtered, and tested exactly as before. Assume readings of 4.7 and 4.6 c.c. for acid and alkali respectively. This indicates an alkalinity of 0.01 per cent., which is satisfactory. For normal operating conditions the limits are 0.01 per cent. acid to 0.02 per cent. alkaline.

The ideal condition of a spent lye for evaporation would be to leave it with sufficient acid to expel all the volatile fatty acids which can be boiled off in the evaporator. Unfortunately this is practically impossible, as the corrosion of the evaporator is marked by acid vapours emanating from a spent soap lye containing only 0.04 per cent. acid.

**Check on Complete Precipitation of Impurities.**—Spent soap lye treatment is most efficient when all matter which can be precipitated has been separated in this form. As a further check on the treatment, three clear filtered samples are placed in separate test tubes. One sample is neutralised, and there is added a drop or two of 10 per cent. solution of sulphate of alumina. If sufficient of this salt has been added, the sample will not show a precipitate. If there is a precipitate formed, more salt should be added to the treatment tank. To the second sample there is added a slight excess of ammonium hydroxide and to the third sample a slight excess of dilute sulphuric acid. If the lye has been properly treated, there will be no precipitate formed in either of these two latter samples or else there will be formed the same amount of precipitate in both.

After the above tests have been made and the spent lye is found to be satisfactory, it is pumped through a filter press. Usually the first filtrate from the press runs cloudy (this is especially true if the lye is cold) and is returned to the treatment tank. The filtered liquor is now ready for evaporation and distillation.

**Test for Arsenic in the Lye before Evaporation.** As glycerol is very difficult to free from arsenic, it is essential for the chemist to test the acid and alum used for arsenic, and reject deliveries containing that impurity.

### Iron Chloride Process of Purification

#### LITERATURE

P. VERBECK. *Seifensieder Zeitung*, 1921, 48, 202.

The purification of the lye by iron chloride or iron perchloride is an old process, which recently has been revived with marked success.

## OBTAINING GLYCEROL FROM WASTE SOAP LYES 17

In one work known to the author the iron perchloride process has been worked for some years, and yields a clarified glycerol much superior to that obtained when the alum process was in vogue.

The following procedure is due to Dr Gerber :—

1. The crude lye is *almost* neutralised with hydrochloric acid and raised to boiling point.

2. Next a 50 per cent. solution of iron perchloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , which theoretically contains 60 per cent. and practically somewhat less) is added to the boiling lye, until a sample withdrawn, filtered, placed in a test tube, and treated with a few drops of a clear ferric chloride solution, yields no precipitate even on standing, but remains quite clear.

3. The lye is now filtered through *wooden* filter presses (iron presses are attacked) into a second treatment tank made of iron covered with bitumen or similar protective coating. The mud which remains in the filter press is usually dark brown in colour, while the filtrate is usually coloured by the excess of iron chloride used.

4. The second treatment tank contains enough caustic soda ( $\text{NaOH}$ ) to neutralise the filtrate. The liquid is heated to boiling and caustic soda solution (of  $40^\circ$  Bé.) added until a filtered sample after boiling and the addition of some further drops of a clear  $\text{NaOH}$  solution gives no turbidity even on standing, but remains perfectly clear.

The liquid now reacts alkaline.

5. The liquid is now pumped through iron filter presses (best with little pressure), the turbid liquid at first flowing being returned to the treatment tank until a perfectly clear filtrate issues from the filtrate press.

The dark green mud left in the press rapidly oxidises to a reddish iron compound.

6. The filtrate is now neutralised with hydrochloric acid until it shows an alkalinity of 0.01 per cent.  $\text{NaOH}$ .

\* Lead-covered tanks and naked iron tanks cannot be used in this process because both metals are strongly attacked by hydrochloric acid.

Iron tanks covered with bitumen or wooden tanks have been used with success.

The iron perchloride process is stated to be dearer than the aluminium sulphate process, although about equal quantities of both kinds of chemicals are used (aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ , has a molecular weight of 558.6, while the equivalent weight of ferric chloride,  $2(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$ , weighs 540.6).

The perchloride process is also stated to refine somewhat better than the aluminium sulphate process.

**Lime Process for Purification.**—Hinckley (*Jour. Soc. Chem. Ind.*, 1907, 26, 597) recommends the following process as well adapted for removing in the form of insoluble salts the soaps of the lower fatty acids, such as formic, acetic, butyric, caprylic, etc.

First there is added to the lyes about 0.5 per cent. of slaked lime as milk of lime. The lyes are agitated with air for thirty minutes and allowed to settle, when the calcium soaps sink to the bottom. The tanks in which the lye is treated or stored are fitted with a draw-off pipe with a swing joint, in order to avoid drawing off anything except clear lye. The lye is filtered into a lead-lined tank, neutralised with hydrochloric acid (the liquor meanwhile being air agitated) until 0.04-0.05 per cent. of free acid remains. The thick scum of fatty and resinous substances which collect on the surface is removed by skimming. It is advisable to add at this stage a small amount of aluminium chloride or sulphate which combines with and helps to remove a part of the fatty soluble acids present. The treated lye is allowed to become clear by subsidence, and is allowed to run without filtering into a second lead-lined tank, where its acidity is neutralised with caustic soda. By leaving the lye 0.01 per cent. alkaline at this point, the albuminous matter is coagulated.

## Garrigue's Process for Glycerol Recovery from Soap Lyes

## LITERATURE

See G. A. MOORE. "Recovery and Purification of Soap Lye Glycerine by the Garrigue's Process." *Jour. Ind. Engineer. Chem.*, 1910, 2, 283.

(Gives a full account which is well illustrated.)

(See also U.S. Patents, 774,171 and 774,172, 1904; English Patent, 24,100, 1904.)

This method presents the following advantages over the preceding processes:—

1. In the preceding processes the volatile fatty acids (e.g., acetic, butyric, caprylic, etc.) are imperfectly eliminated, distilling over with the glycerol even from an alkaline solution, and injuriously affecting the quality of the refined product. In Garrigue's system the volatile fatty acids are almost entirely eliminated *before distilling*.

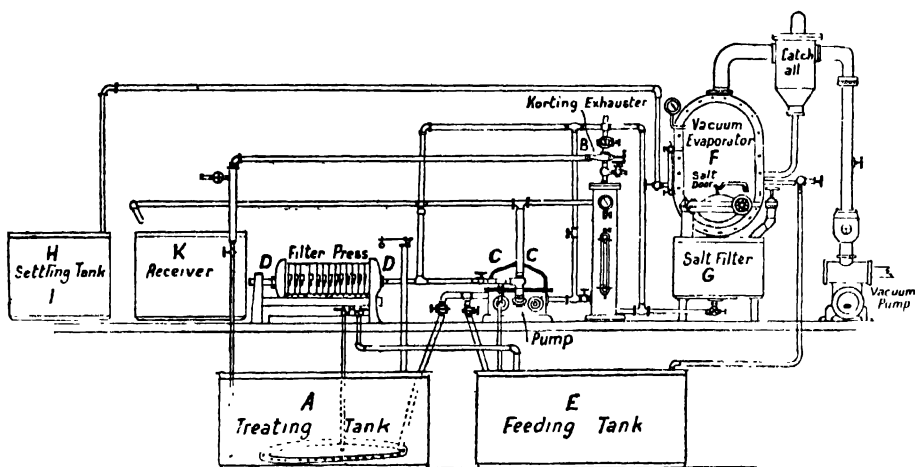


FIG. 5.—Garrigue's Process for Glycerol Recovery for Waste Soap Lye.

2. In the preceding processes the presence of much alkali in the liquor to be distilled (added to the sweet water in order to fix the fatty acids) greatly retards the distillation and does not effect complete separation, since some of the volatile fatty acids distil over with the glycerol, while some glycerol remains behind in the foots. In Garrigue's system so small an amount of alkali is used that it scarcely affects the distillation.

3. In the preceding processes considerable amounts of glycerol foots occur as residues in the still. These contain sometimes over 50 per cent. glycerol, and cannot be economically discarded; the glycerol has therefore to be recovered by mixing with sulphuric acid as described below, and mixing the product with the raw material. Since the foots contain sodium salts of organic acids, these contaminate the glycerol. In Garrigue's system the foots produced are so small in quantity and so poor in glycerol that they can be discarded.

**Details of Garrigue's Process of Glycerol Recovery.**—The soap lye from the soap kettle is run into a storage tank (Fig. 5), where any soap separates out and heavy impurities subside. Next it is run into the treating tank A, and there is added about 0.5 per cent. of aluminium sulphate (or common alum) and sufficient sulphuric acid to nearly neutralise the caustic soda and sodium carbonate present. The contents of the tank are agitated by means of air blown in from a Korting's exhauster B through a perforated coil in the bottom of the tank. The sulphuric acid sets free the insoluble fatty acids before in the solution as soap, while the aluminium present at once precipitates them as insoluble aluminium soaps. After



sufficient agitation, the liquid is forced by the pump *c* through the filter press *D* into the feeding tank *E*. The liquid is now clear. It then passes to the vacuum evaporator *F* and is concentrated (the level in the evaporator being kept constant by a continual introduction of lye in proportion as the liquid boils away). The concentration is carried on until the residual liquid contains about 40 per cent. of glycerol, and about 80 per cent. of the chloride and sulphate of sodium originally present in the liquor have crystallised out and been recovered in the usual way.

Next the liquid is allowed to flow from the evaporator *F* through the salt filter *G* (using a vacuum of 20 in. beneath the salt filter to force the liquid through), and is pumped away to the settling tank *H*.

So far the soluble and volatile fatty acids have remained in solution; these are now removed as follows: The concentrated liquor is pumped from the settling tank *H* into the treating tank *A*, and about 0.5 per cent. barium chloride,  $\text{BaCl}_2$ , stirred in. All the sodium sulphate remaining in the liquor is precipitated as barium sulphate, while any soap still present is decomposed and precipitated as an insoluble barium soap. Now sufficient sulphuric acid is added, sufficient to decompose all the alkali compounds of the volatile and soluble fatty acids, whereby the latter are set free, and in turn are almost completely precipitated as insoluble barium compounds, with the excess of barium chloride remaining in the liquid; thus the volatile acids are removed.

The amount of sulphuric acid required is estimated by withdrawing a sample of liquor, filtering it, weighing off 10 g. into a flask, adding 140 c.c. of distilled water and 1 c.c. of concentrated sulphuric acid, connecting the flask with a Liebig's condenser, and distilling over 100 c.c. Finally, this volume, which contains all the volatile acids, is titrated with standard caustic soda solution, using phenolphthalein as indicator. The organic acidity is then calculated in terms of sulphuric acid, and then the necessary charge of sulphuric acid for the total amount of crude liquor is calculated and run in.

After a thorough agitation the liquid is filtered through the filter press *D* (Fig. 5) into the feeding tank *E*, and is thence pumped into the evaporator *F*, and concentrated until the level of the liquor in the gauge glass remains constant. The volatile fatty acids still remaining (for they are not completely precipitated by the barium chloride) are in part expelled with the water vapour, but part remains to combine with the glycerol as the concentration proceeds, and are retained by it in the form of glycerides. Finally, when the concentration has proceeded so far that the liquid contains 85 per cent. of glycerol, it is discharged from the evaporator *F* into the receiver *K*, and is tested for total acidity by adding excess of standard alkali to a measured sample of the hot glycerol, heating, and titrating back the excess of alkali with standard sulphuric acid. This gives the measure of organic acids still present. The amount of a saturated solution of sodium carbonate (soda ash) required for neutralisation is now calculated and added to the crude glycerol in the receiver *K*, the amount being sufficient to render the mass slightly alkaline. The crude glycerol is now distilled.

According to P. Bertolo Abbali (*Chim. Appl.*, 1919, 12, 24-27), the use of barium carbonate as a purifying agent for glycerine has the drawback that it is difficult to remove the excess of barium. Better results are obtained by the successive use of lime and barium hydroxide. A slight excess of lime is added to the hot sweet waters from the Twitchell or autoclave process, and the liquid allowed to cool completely. The free sulphuric acid is neutralised, and the fatty acids are converted into calcium soaps which carry down with them proteins, colouring matters, and organic impurities. The filtrate from this precipitate is concentrated to 15° B $\acute{e}$ . (sp. gr. 1.116), care being taken that the liquid remains alkaline until the end. During this concentration the calcium sulphate and calcium carbonate are slowly precipitated together with more organic matter. After concentration, the liquid is filtered into an iron vessel provided with a steam coil, where it is heated to boiling and then treated with a slight excess of barium hydroxide (about 6.8 g. per litre) added in small portions. The mixture is boiled for a few minutes, cooled, filtered, heated to boiling in an iron vessel lined with tin, and the excess of barium removed by adding oxalic acid, with precautions to avoid an excess. If necessary, the last traces of barium are removed by adding a little dilute sulphuric acid. Finally, the liquid is cooled, filtered, and concentrated to 28° B $\acute{e}$ . (sp. gr. 1.24).

### Other Processes for Purifying the Soap Lyes

Lime, metallic salts such as ferric chloride, barium chloride, copper sulphate, etc., have been proposed and also used for purifying the lye. The alum treatment, however, is the usual one at present.

A list of some patented processes are appended, which indicates the variety of the methods tried in the past :—

**Blum and Francke's Process** (German Patent, 310,045, 1918).—Soap lyes are concentrated by evaporation and treated with ozone or ozonised air, whereby sulphur compounds are completely oxidised and rendered innocuous, whilst the fatty acids are converted into solid hydroxy acids which can be readily separated. The ozone treatment may also be applied prior to acidification.

*L. Schmidt* (German Patent, 376,643, 22nd April 1922) suggests saponifying fats by alkali in the ordinary way, drying the product, and treating it with a low-boiling liquid in which dry soap is not soluble; for example, acetone, methyl ethyl ketone, methyl acetate, absolute ether, etc. The solution of glycerol so formed is separated from the undissolved matter and the solvent distilled and recovered to be used again, leaving pure glycerol.

**Benjamin Young's Process** consists in first putting the waste lye into capacious evaporating pans or other suitable vessels, provided with coils of pipe made of any suitable metal, through which superheated or ordinary steam is passed. The free and carbonated alkalis (soda or potassa) are next neutralised by adding a solution of sulphuric acid in about the following proportions, namely, one part of water and one part of the sulphuric acid of commerce (68° Bé.), in about the proportion of 2 gals. of the diluted sulphuric acid to every 40 gals. of the waste soap liquor. The solution of sulphuric acid is added to the waste soap liquor in its original bulk, or when it is reduced to about one-half that bulk by evaporation. Superheated or ordinary steam is then passed through the coils of pipe connecting with the evaporating pans, and the waste liquor is concentrated to about one-tenth of the original volume. If any resin or fat is contained in the waste liquor it is admissible to add a slight excess of the dilute acid, and to remove the same—the resin or fat—by straining the concentrated liquor through cloth or any other suitable material made into bags or otherwise, after it has been evaporated to about one-tenth of its original volume. A small quantity of carbonate of lime is then added to the strained liquor, and it is further concentrated by evaporation until upon cooling it assumes the consistency of a syrup or paste, which consists of a mixture of chlorides and sulphates of soda and potassa, sulphate and carbonate of lime, and glycerine. The entire contents of the evaporating vessels are then placed in a centrifugal machine, such as is used for causing the separation of sugar from molasses, which is then set in motion and caused to rotate rapidly on its axis, thereby causing the removal of the glycerine. By this means the greater portion of the salts of soda, potassa, and lime are retained in the interior of the centrifugal machine, the glycerine being thrown off by the rapid rotation of the machine. As the glycerine thus obtained holds a certain quantity of salts in solution, these are separated by distillation.

**George Payne's Process.**—The inventor takes the spent lye resulting from the manufacture of soap and saturates any free alkali present with an acid. He prefers to use sulphuric, hydrochloric, or nitric acid. He then takes a solution of tannin or tannic acid, and adds this to the spent lye after being neutralised by the acid. This solution should contain about one part by weight of tannin or tannic acid to about ten parts by weight of water. The addition of the solution to the lye is continued until it ceases to precipitate any albuminous or gelatinous matter.

The precipitate which is thus formed is separated by filtration, or is allowed

to settle. The remaining liquid consists chiefly of raw or impure glycerine and chloride of sodium. The solution should be warmed, as experience shows that heat facilitates the formation and separation of the precipitate. In some instances the solution may be found to be slightly acid; if so, it must be neutralised by the addition of milk of lime. The clear liquor, which is a mixture of glycerine and spent lye, is next heated to expel the water, thereby concentrating the mixture and removing from the same a large quantity of the salts, which will crystallise out during the process of evaporation. For this purpose heated air, superheated steam, or the direct heat of the fire may be employed.

By this process a concentrated solution of glycerine is obtained containing about 10 per cent. of salt, and the glycerine may be separated by distillation and refined in the usual way. The inventor says that "the glycerine obtained by this process may be more easily refined by distillation than that obtained by any known process."

**Versmann's Process.**—The object of this invention is the recovery of glycerine from soap lyes, and its more or less complete separation from chloride of sodium, carbonate of soda, and caustic soda. A large percentage of these salts is separated by simply boiling down the soap lye and raking out the salts as they become insoluble. The concentrated solution is then allowed to cool, after which carbonic acid gas is passed through it until the whole of the carbonate and caustic soda is converted into bicarbonate of soda, which being much less soluble in glycerine than either the carbonate of soda or caustic soda, may readily be removed by filtration or other convenient means.

The inventor sometimes commences by passing carbonic acid gas through the original soap lye, but he finds it more convenient to first reduce the bulk of the liquid by boiling down, thereby separating large quantities of the salts, and then treating the liquid with carbonic acid. The liquid from which the bicarbonate of soda has been removed is very rich in glycerine, but it still retains sensible quantities of chloride of sodium and other salts, the presence of which may act injuriously in the subsequent applications of the glycerine to certain purposes. These salts are separated by submitting the liquor, either hot or cold, to the process of "osmose," in an apparatus known as the "osmogene," such as is used in the separation of saline compounds from solutions of beetroot sugar. By this process nearly all the salts are separated from the glycerine. But as the latter becomes diluted with water it may be concentrated by evaporation, when it will be ready for the market as crude glycerine.

**O'Farrell's Process.**—The spent lyes are evaporated immediately they are drawn off from the soap pan by fire heat or dry steam applied by any suitable apparatus, till a saturated aqueous solution of common salt is obtained, and this saturated solution is used for the purpose of separating the glycerine from a fresh portion or second charge of soap, when the spent lye obtained from this fresh portion or second charge is evaporated, and this is again returned to the soap copper for the purpose of separating the glycerine from a third charge, and the lye obtained is evaporated as before. The process is repeated until the quantity of glycerine present in the solution is sufficiently concentrated to be economically separated.

Having by this means obtained the maximum amount of glycerine in the minimum volume of spent soap lyes, the inventor proceeds to evaporate the solution till as much salt as possible crystallises out, when the glycerine is dissolved out from the residue by means of methylated spirit or other suitable liquid, or the glycerine may be separated by distillation *in vacuo*.

**Thomas and Fuller's Process.**—The spent or partially spent lyes are first evaporated until nearly all the salts are deposited; the resulting liquor, which is strongly impregnated with glycerine, is then boiled with an excess of fat or fatty

acids, which readily combines with the soda salts, and removes all salts which may be in suspension in the liquor. The solution is then filtered and subjected to distillation to recover the glycerine, or the spent lyes may be treated with quicklime to convert the carbonate of soda into caustic soda, and after filtration boiled to concentration, and then fat or fat acid may be added to remove the soda and such salts as may be in suspension. The method described above, however, is preferred, using simply concentrated lyes and a fat acid as the more effectual means of clearing the liquor of salts.

**Allan's Process.**—The inventor first neutralises the spent lyes with any mineral acid with agitation. After settling, he adds a solution of alum, chloride of lime, or crude pyroligneous acid, stirring thoroughly. If preferred, he evaporates to nearly "salting point" before adding any of the substances mentioned above, and allows the precipitate to deposit. After settling he draws off the clear liquor and evaporates it to a concentrated condition in pans (to which the heat is only applied at the sides), or in shallow pans with sloping bottoms, to which the heat is applied. The liquor is then distilled in a glycerine retort heated by superheated steam from within, and provided with an exit pipe at the bottom, which carries off the precipitated salt as it accumulates.

**Lawson and Sulman's Process** consists in first evaporating the lyes to a density of from 1.14-1.16, and allowing the solution to cool. The salt liquor being thus concentrated, the residual soapy matters remaining in solution are rendered insoluble, and, rising to the surface, may readily be removed by skimming or otherwise for further use. To remove the albuminous matters remaining in the liquor it is first heated, after which a salt of chromium sesquioxide is added, which is capable of tanning or rendering albumen insoluble. The quantity of the chromium salt added will depend upon the percentage of albuminous matter existing in the lye. The albuminous matters thus rendered insoluble by the addition of the salt are precipitated and removed.

The removal of these matters at this stage prevents their decomposition by further evaporation, and thus a purer and more concentrated glycerine of better colour than usual is obtained. The alkalinity of the liquor is at the same time neutralised by a suitable acid.

The inventors remark, "A very convenient method of effecting our invention, so as to obtain these two results, *i.e.*, the tanning of the albuminous matters and the neutralisation of the alkalinity, is to use the waste liquor resulting from the bleaching of tallow or other fats or oils (chrome liquor?). For a lye such as the above we may add the bleaching liquor in the proportion of, say, 1-3 gals. for every 100 gals. of original lye; but this must depend entirely on the strength and colour of the lye. When treating highly-coloured lyes, we add a proportion of free chromic acid to the waste liquor, which, by the oxidation and destruction of the colouring matters, is reduced to a salt of chromium sesquioxide capable of removing the albuminous matters as above."

The quantity of chromic acid will necessarily vary, but for the above quantity of lye we should say about  $\frac{1}{2}$  lb. of bichromate of potash added to a mixture of  $\frac{3}{4}$  lb. of sulphuric acid in 2 lbs. of water, and add this mixture in the proportion of 5-20 lbs. to every 100 gals. of lye, according to circumstances. We now treat the liquor with a small excess of calcium carbonate (say, for example, 1-2 gals. "cream of whiting" to 100 gals. of lye), and maintain at a boiling temperature for a short time. This precipitates the whole of the chromic salts, and neutralises any slight proportion of acid remaining. The chromic oxide contained in the resulting precipitate can be recovered for another operation in any suitable and well-known manner. The resultant liquor obtained by removing the precipitate by subsidence or filtration will be found clear and almost colourless. It is then concentrated by further evaporation, which causes the gradual separation of the salt, which can be again used in the manufacture of soap.

The crude glycerine finally obtained is of greater purity and better colour than usual.

**Victor Clolus's Method.**—To effect a separation of the various bodies for commercial purposes, and especially to extract the glycerine from spent lyes, the inventor first saturates the lye, when cold, with hydrochloric acid. The solids are precipitated and collected; the neutral clear liquid is evaporated in any suitable heating apparatus. By degrees, as the evaporation proceeds, the salt is precipitated and is removed, subjected to the action of a turbine, and washed. In most cases this salt is sea-salt in a nearly pure state. The evaporation is arrested when the liquid has arrived at a density of about  $32^{\circ}$  Bé. At this point the glycerine contained in the lye still contains considerable quantities of salt in solution, the greater part of which is eliminated by the following treatment; that is to say, the glycerine liquid, at about  $32^{\circ}$  Bé., is poured into any suitable vessel and hot air is blown into it, or the liquid is otherwise heated and cold air blown into it. The air so heated, or heated by the glycerine itself, gradually eliminates the last traces of water in the glycerine, and salt is constantly precipitated, as the latter is very slightly soluble in anhydrous glycerine. To eliminate the water evaporation *in vacuo* might also be effected, but would be more expensive. As the final result, highly concentrated glycerine mixed with salt crystals is obtained. A turbine is used for eliminating the salt, which is systematically washed, and the water used for the washing is again treated.

The glycerine, thus purified by one or the other of these two processes, contains only a very small quantity of sea-salt in solution, and may be distilled. The inventor also adopts another method when he desires to obtain the carbonated or caustic salts of soda in the condition of carbonates, instead of transforming them into chlorides by means of hydrochloric acid. For this purpose he evaporates the lye and introduces into it carbonic acid, so as to convert the caustic soda into carbonate. When the liquor indicates about  $25^{\circ}$ , he allows the lye to cool, when he introduces an excess of carbonic acid whereby bicarbonate of soda is formed, which is only slightly soluble, especially in a glycerine solution of salt. The greater part is precipitated and is eliminated by means of a turbine. The bicarbonate is transformed into carbonate by calcination. The glycerine liquid which leaves the turbine is treated as before. If it is desired to obtain glycerine more free from salt, the operation is performed as follows: The glycerine concentrated by air blown into it, or *in vacuo*, is treated with hydrochloric acid added in excess, either in a gaseous state or as a liquid. Sea-salt, being almost insoluble in an excess of hydrochloric acid, will be precipitated in fine crystals, and is eliminated by means of a turbine. The excess of hydrochloric acid then contained in the glycerine is eliminated either by blowing air into the same or by an excess of oxide of lead.

**Benno, Jaffé, & Co.'s Method.**—According to this process the inventors do not use common salt for separating the soap from the lye, but employ in lieu thereof an alkaline sulphate. The alkaline sulphates, especially the sulphate of soda, act upon the soapy liquor in the same manner as common salt, but there will be no difficulty in subsequently separating such sulphate from the glycerine. The spent lye obtained in eliminating the soap by means of sulphate of sodium has an alkaline reaction, and is therefore first neutralised by the addition of hydric-sodic sulphate; it is then filtered and ultimately evaporated. In the process of neutralising the spent lye the hydric-sodic sulphate is transformed into sulphate of soda by the caustic soda contained in the spent lye. When the liquid is evaporated the sulphate of soda separates in crystals, and is thus recovered as a by-product. The sulphate of soda, which has been introduced for the purpose of separating the soap from the lye, is also separated, and if properly purified can be used again for eliminating soap from the lye. The liquid remaining after the crystallisation is glycerine

containing a slight proportion of impurities, and can be further purified in the usual manner, as for instance by distillation.

**Barbet and Rivière's Processes** (see French Patents, 338,962, 1903; 367,752, 1906; also *Jour. Soc. Chem. Ind.*, 1907, 26, 426).—Rivière processes to obtain glycerol from soap lyes and distillery products (vinasses) by the use of hydrofluosilicic acid are as follows :—

In their first patent Barbet and Rivière proceed as follows :—

The liquid is treated with silicofluoric acid to precipitate the salts of potassium, sodium, etc., the precipitate is washed, and the glycerine separated from the filtrate and washings. The addition of alcohol before the filtration increases the insolubility of the silicofluorides. In the case of the products of alcoholic fermentation (vinasses, etc.), the liquid is first concentrated to 10° or 12° Bé. in the presence of lime or calcium carbonate, and then filtered, and the filtrate treated with silicofluoric acid, the excess of which is neutralised with sodium or calcium carbonate. The liquid is next filtered, with or without the addition of alcohol (which is subsequently evaporated), the clear filtrate concentrated, and the residual crude glycerine purified, *e.g.*, by osmosis, as described in French Patents, 323,373 and 330,939 (see *Jour. Soc. Chem. Ind.*, 1903, 502, 1101).

In the second patent Rivière proceeds as follows :—

Salts of sodium and potassium in the crude glycerine are precipitated by means of hydrofluosilicic acid, which is subsequently recovered from the fluosilicates. The free hydrochloric acid in the filtrate, resulting from the decomposition of the sodium chloride, is separated either by distillation with steam and then saturated with lime, or it is converted into an ester by treatment with alcohol before distillation; or is precipitated as lead chloride by means of lead fluosilicate. The precipitated sodium and potassium fluosilicates may be converted into carbonates by treatment with sufficient lime to form the corresponding silicates and calcium fluoride, after which the silicates are decomposed by means of carbon dioxide and the resulting carbonates separated from the precipitated silica. The latter is dissolved in hydrofluoric acid to form hydrofluosilicic acid, or is converted into lead fluosilicate. All these different operations are carried out in autoclaves to which, when required, condensers and absorption vessels are attached.

In a later patent (see *Jour. Soc. Chem. Ind.*, 1907, 26, 421) the hydrofluosilicic acid in the precipitated alkali fluosilicate is recovered by treatment of these salts with lime, preferably partially carbonated, in an autoclave, or with hydroxides of barium magnesium, etc., or by the action of acids or alkali bisulphates.

If phosphoric or sulphuric acids or bisulphates be used, the resulting phosphates or sulphates may be boiled with barium carbonate and water either in an autoclave or under ordinary pressure to convert them into potassium or sodium carbonates, which may be separated in a state of sufficient purity for commercial products. In treating distillery by-products, ammoniacal nitrogen may be removed by neutralising the substance with lime and heating the decanted vinasses in an autoclave with magnesia or barium hydroxide. The glycerine solution after removal of ammonia and alkali salts may be concentrated, and treated with a solvent such as alcohol, which also precipitates mineral and organic matters; the glycerol is removed by distillation. Pure ethyl acetate may take the place of alcohol as a solvent, and the portion that remains in the aqueous layer may be recovered by distillation.

**Process for obtaining Pure Glycerine from Liquids containing it** (see *Farbenfabr. vorm. F. Bayer und Co.*, Leverkusen, German Patents (A), 303,805, 17th June 1917; and (B) 305,174, 6th July 1917).

(A) The liquid is treated with lead compounds, such as litharge or lead  
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hydroxide, in order to precipitate an insoluble lead-glycerine compound. This is separated and decomposed by any suitable means, *e.g.*, with hydrogen sulphide, sulphuric acid, or carbon dioxide.

(B) The lead-glycerine compound may be decomposed by heating with water under pressure. A solution containing 16 per cent. of glycerine is thus obtained ; the lead oxide is precipitated in a heavy form and can be easily removed to serve for the precipitation of a further quantity of glycerine from crude glycerine or spent wash.

## CHAPTER IV

SOAP LYE GLYCEROL (*continued*).—EVAPORATION OF PURIFIED SOAP LYE TO CRUDE GLYCEROL—GENERAL PROCESS OF CONCENTRATION DESCRIBED

## LITERATURE

E. BRIGGS. See preceding chapter, and especially "The Distillation of Glycerine" in Sydney Young's *Distillation Principles and Processes*. Macmillan, 1922.

## General Process of Evaporation

THE purified and filtered soap lye resulting from the preceding operations should now be free from fatty, resinous, and albuminous matter. The lye should consist of an aqueous solution of salt (sodium chloride), a small amount of sodium carbonate and practically pure glycerol, and possess a specific gravity of 1.08-1.14. This liquor is now converted into *crude glycerine* by concentration, which eliminates the water and causes most of the salt to be deposited.

The liquor begins to deposit salt when the specific gravity of the liquor at 15.5° C. reaches 26° Bé. (44° Tw. = sp. gr. 1.220). When evaporation is carried beyond this stage, salt is deposited, whilst the specific gravity and percentage of the glycerol increases.

The concentration was originally carried out in *open pans* heated by fire or waste combustible gases. In the bottom of each pan was placed a vessel in which the salt deposited, and this dish was lifted out at intervals by means of an overhead crane and the contents emptied and washed. The concentration was continued until the temperature of the liquor reached 149° C. (300° F.), when the liquor was allowed to stand.

This liquid contained 80 per cent. glycerol and from 8-10½ per cent. of salt. Thus arose the present standard for crude glycerine.

Concentration in open pans, however, has now been long superseded by *evaporation in vacuo*.

The low *initial cost* of the old open pans was obtained at the expense of efficiency. The modern vacuum plant entails a high capital cost, but this is more than compensated for by increased economy of working.

The **Vacuum Evaporator** consists of a sheet-iron boiler heated internally by a series of steam-heated pipes, while a vacuum pump maintains inside the vessel a vacuum of between 18 and 28 in. Under the diminished pressure the water boils off rapidly, leaving the glycerol behind. As the liquid concentrates salt is deposited. It falls between the heating pipes of the boiler and collects at the bottom, whence it is from time to time withdrawn through doors placed at the bottom of the vacuum chamber.

The loss of glycerol by evaporation is extremely small (2-3 per cent.) when the



operation is carried out under a vacuum of 26 in. and with steam at a low pressure. The liquid is boiled until a sample of lye withdrawn shows a density of 30° Bé. (53° Tw.) at 15° C. (59° F.), when it consists of 50 per cent. glycerol, while most of the salt has been deposited and withdrawn. Then the liquid is sucked into a storage tank situated below the evaporator, allowed to cool, separated by filtration from any precipitated salt, passed into a second evaporator of a similar type but smaller, and the evaporation carried on until the proportion of glycerol reaches 80 per cent., the salts and water varying between 10 and 12 per cent. (It is, however, possible to prepare in some of the evaporators described below crude glycerol containing 86 per cent. pure glycerol. No useful purpose is served by concentrating beyond 83 per cent., and it is very expensive to raise the percentage to 86 per cent., so that this is seldom done in practice.)

In Germany it is the practice to place the salt thus removed in a centrifugal and wash with water until it contains only about 0.25 per cent. of glycerol.

The final liquor now registers 60° Tw. (33.3° Bé.=sp. gr. 1.30) at 60° F. (15.5° C.). The crude glycerol is now withdrawn to a tank, the excess of salt present allowed to deposit, and finally the liquor is run into a storage tank, whence it can be passed into the still and distilled *in vacuo* as described below.

According to Hinckley (*Jour. Soc. Chem. Ind.*, 1907, 26, 596), in the evaporators a vacuum of 25-27 in. should be maintained. The evaporation is best carried on with exhaust steam until the lye is saturated with salt (at 25° Bé.), beyond which live steam at 60-70 lbs. pressure should be used.

He also states that tube evaporators are only efficient when the tubes are kept clean, which is accomplished by boiling out the evaporator often with fresh lye. Iron tubes must be scraped at least once a month to remove scale. Dash plates suspended in the top of the evaporator prevent much throwing over of the boiling liquor. What does pass into the vapour pipe is caught in cylindrical drums called "catch-alls" and run back into the vacuum. Wet vacuum pumps are usually used.

Evaporation carried out under a vacuum or reduced pressure has undoubtedly proved itself more economical than any other system.

This is due to the fact that liquids change to the state of vapour at low temperatures when heated under reduced pressure.

For this reason liquids decomposing under high temperatures can be easily handled and, what is especially important, the heat supply can be generally obtained from a waste source, such as exhaust steam or flue gases.

The system consists, briefly, in enclosing the liquor in a sealed vessel having outlet only for the vapour or steam, conducting this to a condenser and removing the liquefied vapour as it is formed. Heat is applied to the liquor from an external source, its temperature being somewhat higher than the boiling temperature of the liquor under reduced pressure. The heat flow resulting through the dividing walls of the vessel goes to make up the latent heat of vaporisation and drives off a portion of the liquor as vapour. The vapour is conducted by pipes to the condenser where the condensible part is reduced to liquid form, its heat being extracted by some cooling medium, usually cold water. The function of the air pump or vacuum pump is to remove the air or gases incapable of condensation, while incidentally it may remove the condensate as well.

Fairly good rates of boiling can be maintained with a difference of temperature of 15° C. between the heat supply and the boiling liquor. Usually, however, a very much greater temperature difference is available. For example suppose a liquid boiling under 27 in. vacuum has a temperature of 55° C. and the heat supply is by exhaust steam at atmospheric pressure, temperature 100° C. Obviously 45° C. is the drop causing heat flow, and the boiling rate will be correspondingly high.

Such an evaporator is commonly called a single effect. If steam is the heating medium, then the limit of evaporation is reached per lb. of steam supply, when all of the latent heat of the steam is given up to form latent heat of vaporisation,

that is, when the evaporator feed is at the boiling temperature, it then approximates to 95 per cent. of the dry steam supply.

If the heat supply to such a vessel is provided by vapour from another similar vessel, then the heating system forms a condenser for the heat supply. In this way we obtain two vessels in series, so that one may say the steam is being used twice over. Taking our previous case with atmospheric steam supply and temperature drop of  $45^{\circ}\text{C}$ . between that and the condenser, the drop between the successive vessels is halved, *i.e.*, it is now  $22\frac{1}{2}^{\circ}\text{C}$ ., so that the evaporation per square foot or per square metre of surface will be reduced. Hence for the same amount of evaporation we may say, roughly, the surface is doubled, and the steam used is halved, while the condensing water is also halved.

A continuance of this principle leads to the use of triple, quadruple, and even up to octuple effect, the number of vessels in series being limited only by the extreme temperatures which are available, and the drop required between successive vessels. It is to be noted that the advantage of extremely low boiling temperature is only obtained in the last vessel, however, as the first of the series may even be boiling under a pressure considerably above the atmosphere.

**General Requirements of Modern Evaporating Plant.**—A modern vacuum *evaporator* should fulfil the following requirements :—

1. The heating surface should be arranged to give a *rapid circulation*. A large heating surface will not compensate for lack of rapid circulation, because the deterioration of a large surface with poor circulation is much more rapid, and consequently more expensive in upkeep, also the heat transmission is much better with a rapid fluid velocity. The design to give *good condensation on the tubes* is as important as that designed to give *evaporation*, since the one operation cannot be done without the other ; so that, if the removal of condensation or the access to the tubes for steam is deficient, all attention to such an obvious advantage as good circulation goes for nothing.
2. Vapour chambers must have ample volume, and be fitted with baffles to direct stray drops or particles back to the boiling liquor.
3. Ample provision must be made in the way of sight glasses and gauges. Air valves and other fittings must be provided to avoid a multiplication of small air leaks which are difficult to detect.
4. Save-alls should be placed where they will return the entrainment back to the pan before any condensation of vapour has occurred. They should offer as little obstruction to the vapour as possible, consistent with effective separation.
5. Large vapour pipes are advantageous in that the velocity of the vapours is kept low, thereby causing a negligibly small drop in pressure (and consequently temperature) between the vapour chambers and the succeeding steam chambers or condenser. The liability to priming is also reduced.
6. The condenser and air pumps should be considerably in excess of the normal condensing requirements ; in this way only is it possible to maintain evaporative efficiency over an extended period.
7. The designer must know the available steam pressure, the temperature of the cooling water, and the boiling temperatures of the liquid to be handled. Given these details the most suitable plant can invariably be left in the hands of the maker or consultant.

### Types of Modern Plant for Concentrating the Lye and Separating the Salt

The various types of modern plant used for the purpose of concentrating *in vacuo* will be described in the following chapters.

There are several main types of tube evaporators used : (1) *One made entirely*

of iron and *with vertical heat pipes*. The liquor circulates in the tubes and the steam outside.

The **Foster Evaporator**, **Scott's Evaporator**, and **Blair, Campbell, & M'Lean's plant**, etc., are of this type and are described below.

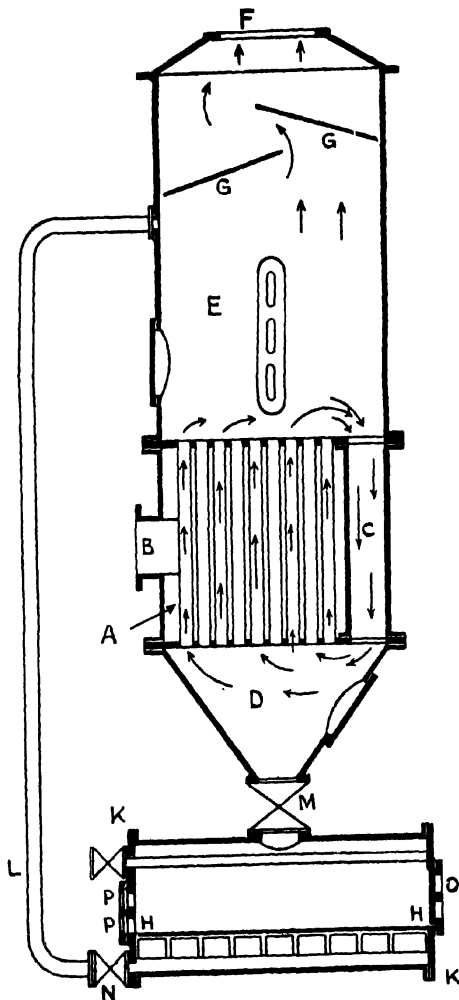


FIG. 7.—Foster's Waste Lye Evaporator.  
(Fullerton, Hodgart, & Barclay Ltd., of Paisley, Scotland)

(2) In the other type the evaporator is made of iron and is fitted with *horizontal brass tubes*, the liquor circulating *outside* the tubes and the steam within.

The well-known **Swenson Evaporator** is of this type.

(3) The **Kestner Salt Evaporator** is of a different type to either of the varieties, and is described below, being "Film" evaporator.

A typical modern plant is the—

**Foster's Soap Lye Evaporator.**—The diagrammatic section shown in

SEC. I.

Fig. 7 illustrates the main characteristics of the Foster evaporator vessel. The heating steam is admitted to the calandria *A* through the opening *B*, and there is a positive unidirectional circulation of the boiling liquor through the tubes, the down-comer *C*, and the bottom cover *D*, as indicated by the arrows. Vapour liberated in the chamber *E* passes at a low velocity through the large diameter opening *F*, and thence to the condenser and air pump by way of the save-all and vapour piping. Baffle plates *G* are fitted to break up foaming. The salt, precipitated during the process of concentration, is collected on a special filter bed *HH* in the salt box *KK*, and the filtered liquor is returned to the vessel through the pipe *L*.

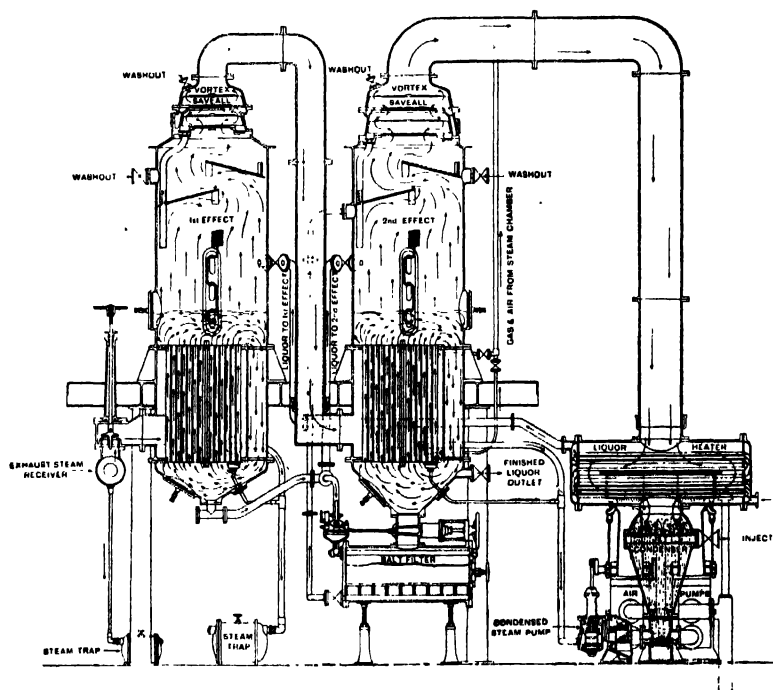


FIG. 9.—Section of Foster's Patent Evaporator.

This illustration shows the principle of double effect evaporation applied to the concentration of soap-makers' spent lye for the production of crude glycerine and the return of dry salt. This liquor is admittedly one of the worst to handle in concentration.

Connections are provided on the salt filter for the removal of surplus glycerine from the salt by a weak liquor wash and for the drying of the salt by steam. The filter may be isolated from the vessel by means of the sluice valve *M* and cock *N*, and when the vacuum is broken by an air cock, the dried salt is removed by means of the door *O*, ready for use in the soap pans. Sight glasses *PP* are fitted so that the contents of the filter are under observation. Since the vacuum is broken only in the salt box, the process of evaporation goes on continuously in the vessel until liquor of the desired glycerine content, usually about 80 per cent., is obtained.

In the multiple effect plant, vessels, similar to the foregoing, are placed in series, and so connected that the vapour liberated from the boiling liquor in the first vessel passes into the steam chamber of the second vessel, and so on through the series. Throughout the series of vessels there is a stepped temperature drop with corresponding degradations in vacua, and consequently the heat in the vapour from one vessel suffices for the boiling of the liquor in the vessel next in order.



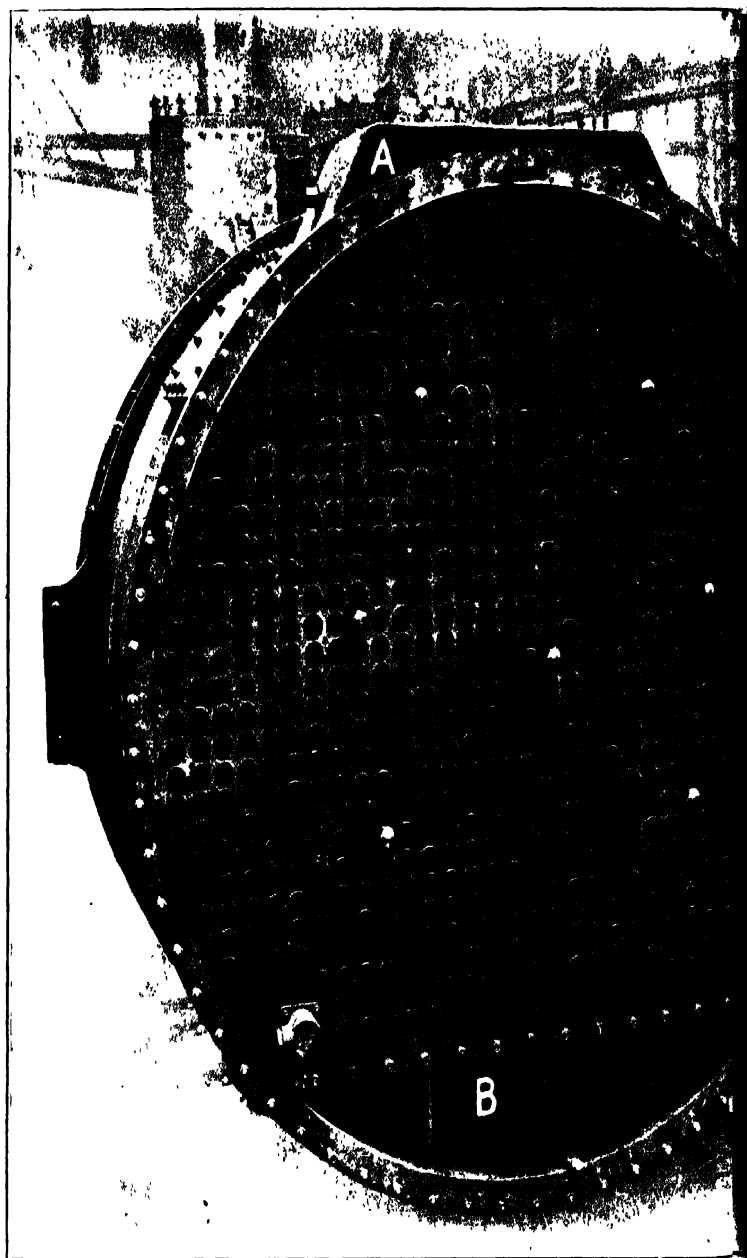
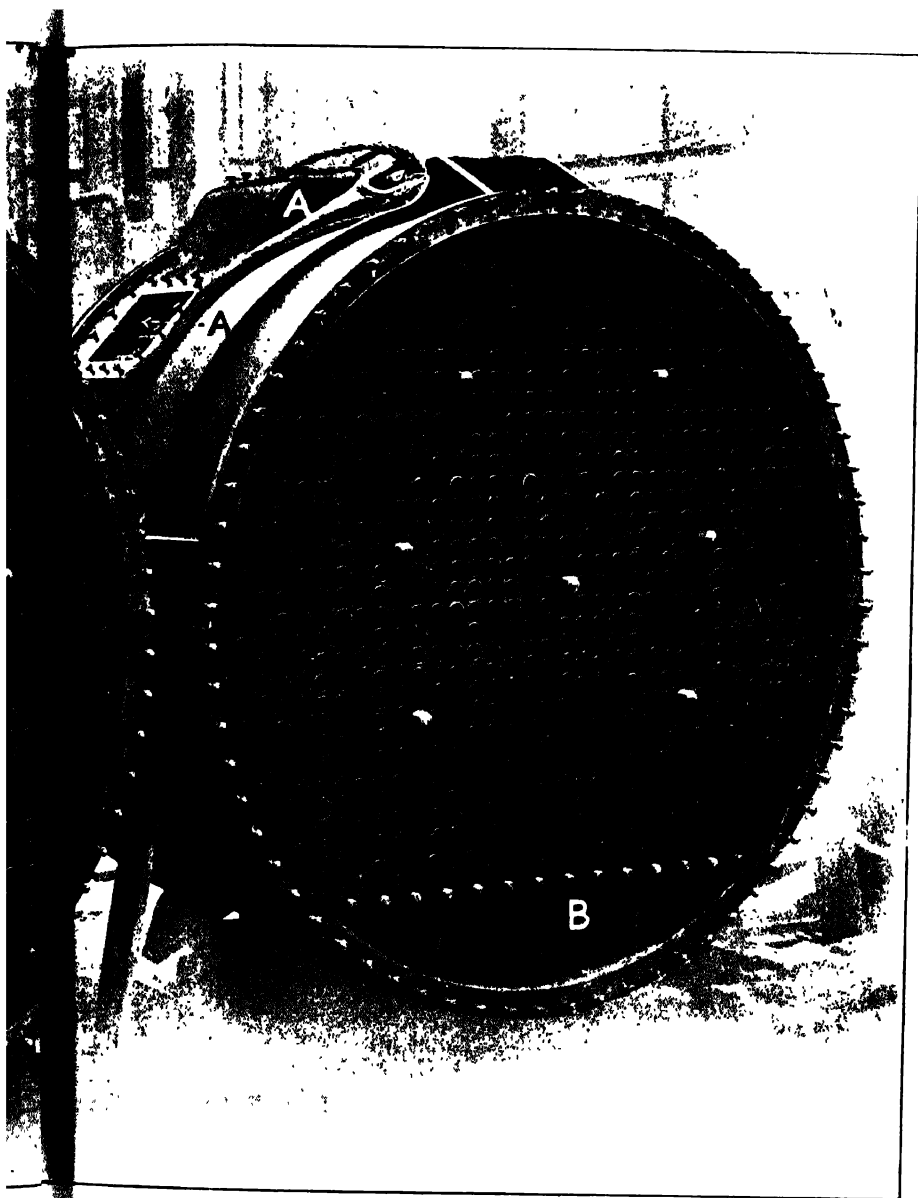


FIG. 8 --Calandria of IV

A. Wide steam inlet and arrangement of tubes, thus securing distribution of steam over all the heating surface.



of Waste-Lye Evaporator.

of B Downcomer or circulating passage of large section and remote from steam entry, hence promoting vigorous circulation

SEC. I.

| To face page 30.





For soapworks the Foster evaporator is arranged to utilise economically exhaust steam at a maximum back pressure of about 10 lbs. per square inch, and owing to the limited temperature range thus available and the high boiling temperature of "crude" glycerine, single and double effect plants only are used for the concentration of the soap lye.

Fig. 9 gives, with considerable detail, a sectional arrangement of a complete Foster double effect installation, and illustrates points in design to which the makers, Messrs Fullerton, Hodgart, & Barclay Ltd., Paisley, Scotland, give special attention. These salient points may be summarised as follows :—

1. The downcomer, or circulating passage, formed in the casting of the steam chamber, is situated at the side remote from the heating vapour inlet, where the lowest temperature prevails. This design results in a unidirectional circulation of the most vigorous type, and thus promotes efficient heat transmission, and tends to prevent the rapid formation of scale on the tube surfaces.

2. The steam, or heating vapour, is admitted to each calandria by way of a very wide, splayed opening, augmented, in the case of very large vessels, by symmetrically placed side inlets. Good distribution of steam is thus ensured throughout the entire heating surface of the tubes.

3. A special syphon drainage arrangement is fitted to each steam chamber in order to avoid the evil effects of the accumulation of water on the bottom tube plate.

4. Free vapour liberation is promoted by the provision of specially high vapour chambers, fitted with baffle plates to break up foaming, and Vortex type save-alls from which drainage is returned directly to the boiling liquor by internal pipes.

Manholes in the vapour chambers and bottom covers afford easy access to the top and bottom of tubes, and wide angle sight glass frames render the interior of the chambers easily visible.

5. Vapour pipes are of very large diameter, so that vapour velocities are kept very low and risk of priming thus reduced to a minimum.

6. A separate auxiliary pump is provided solely for the removal of the water of condensation from the second effect steam chamber which is under vacuum. This arrangement avoids a common defect of many multiple effect plants in which the drainage of the calandrias, irrespective of the degree of vacuum obtaining therein, is accomplished by pipes with control valves leading to the main condenser, where a totally different and higher degree of vacuum is maintained. If the control valves are adjusted to give passage to the water only, then a non-conducting blanket of air and non-condensable gas must form in the calandrias and hinder heat transmission. If, on the other hand, the valves are opened sufficiently wide to pass the gases, the expansion of these entering the higher vacuum of the main condenser gives the vacuum pump increased duty, and the desired vacuum in the last effect chamber is more difficult to maintain. In addition, the connecting of each calandria to the condenser tends to disturb the balanced action of the plant by affecting the relative vacua in the vessels and the corresponding heat drops.

For drainage purposes each steam chamber of a multiple effect should be recognised as a condenser, and provided with a separate pump to remove the water and gases at the pressure of their formation.

Fig. 8 is taken from a photograph of two very large diameter Foster calandrias. The steam inlets are clearly shown at A, and the downcomer at B.

**Scott's Apparatus** (see English Patent, 15,159, 1899).—Fig. 10 shows **Scott's Crude Glycerine Recovery Plant** both in plan and section. Fig. 11 shows a general view of the plant. The apparatus consists of three tanks, a filter press, and a steam pump.

The soap lye after separating of crude soap, etc., is placed in the tank 1 (fitted

with air mixture and live steam coils, as above described), and treated with alum in the ordinary way in order to precipitate soap, albuminous matter, etc.

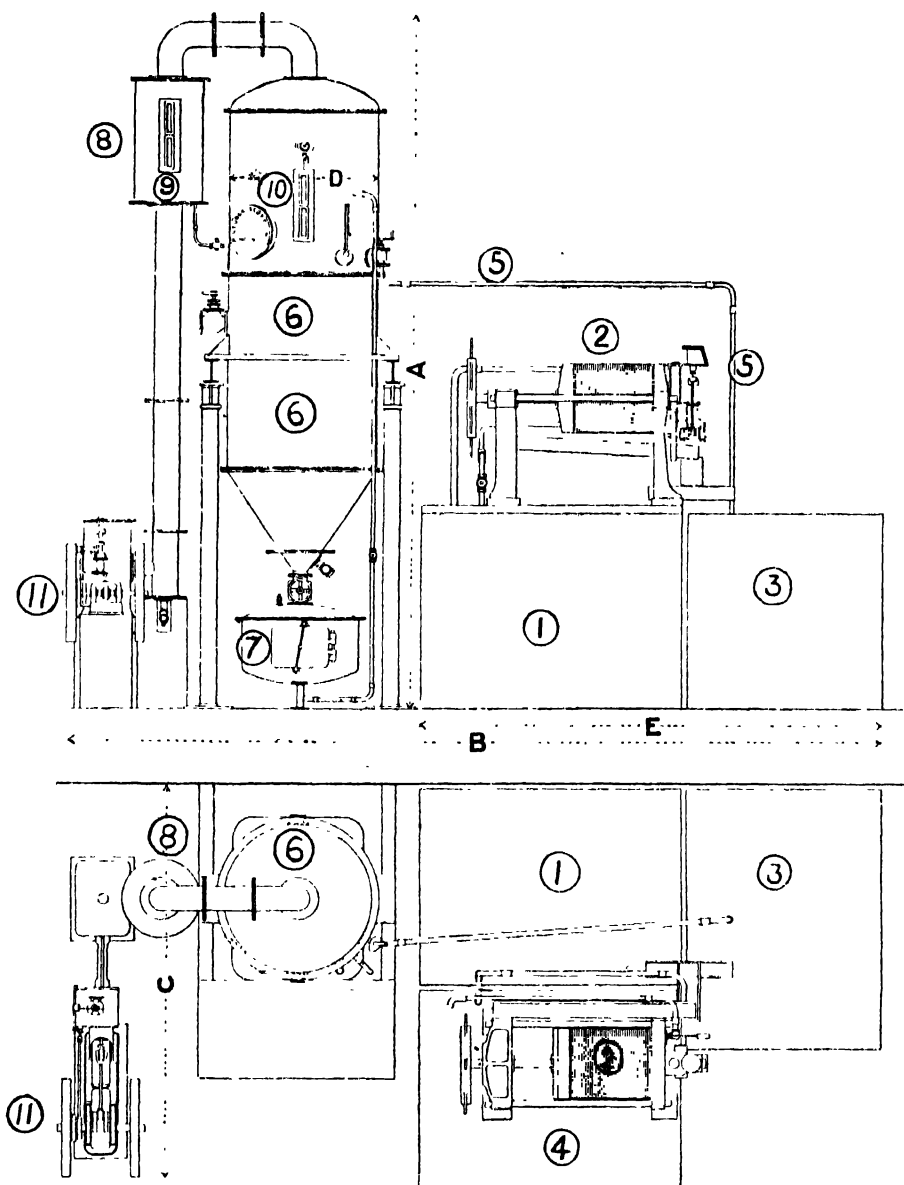


FIG. 10. —Scott's Crude Glycerine Recovery Plant in Plan and Section.

The liquor, after boiling and well agitating with compressed air, is pumped through the filter press 2 and the clear filtrate runs into the second treating tank 4, where it is neutralised. The liquid is then pumped again through the filter press into the tank 3, whence it is sucked (by means of the vacuum) into the *vacuum evaporator* 6 for evaporation.

Some large works proceed as follows :—

The soap lye is run into a mixing tank of a special shape. It is agitated by means of arms, and is provided with a live steam perforated coil at the bottom.

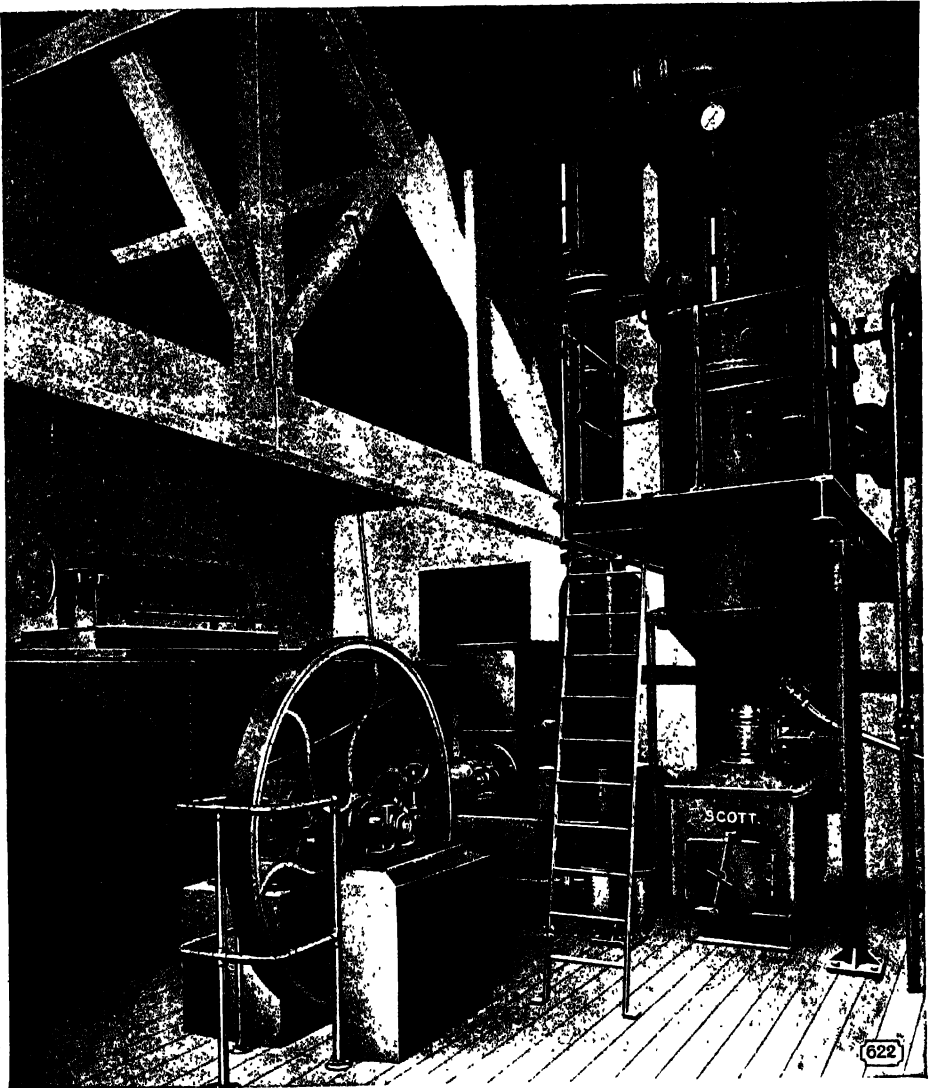


FIG 11.—General View of Scott's Crude Glycerine Recovery Plant for Waste Soap Lye.

Showing salting-out box, pumps, treating tanks and filter press.

The alum is added, and the whole is heated with steam and thoroughly agitated by means of the paddles. The liquor is then allowed to settle and then pumped through the filter press into the settling tank. This method is said to work more rapidly and easily than the usual method.

The purified glycerine solution, freed from soap and albuminous matter, is

now in a condition to be placed in the vacuum evaporator for concentration in order to remove the salt.

The **Scott Evaporator** (Figs. 10, 11, 12, and 14) is of the pan type, the heating system being composed of a number of vertical tubes of *two diameters*, so arranged that a very vigorous and evenly distributed circulation is attained without mechanical aid, thus preventing the salt caking on the heating tubes and destroying the efficiency of the heating surface. *Exhaust steam* may be used for heating up to 80 per cent. concentration of glycerine. Loss by boiling over ("entraining") is guarded against by the fact that the circulating is itself a froth destroyer. Also there is provided a special catch vessel with internal baffles and an arrangement for trapping any liquor which comes over (fixed at 8).

The view glasses 9 and 10 allow one to see what is taking place inside the evaporator. The *vacuum* is produced by a vacuum pump on the displacement principle, the plunger working under a body of water and in conjunction with a

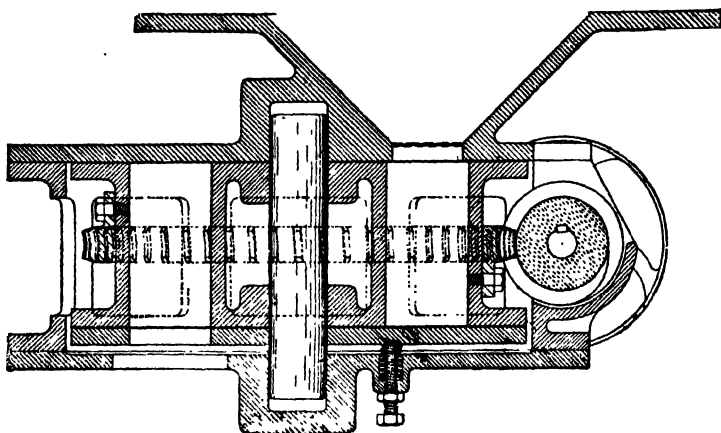


FIG. 13.—Scott's Automatic Salt Discharger.

jet condenser, the water from which is also removed by the pump, thus avoiding the necessity of a special water pump or a barometric column.

The glycerine liquor is concentrated in the vacuum pan (above described) until it contains 80 per cent. glycerine and about 10 per cent. of salt. The salt crystallises out and is removed at the bottom in two distinct ways.

For the *smaller sizes* a salt box 7 (Fig. 10) is fitted to the bottom of the evaporator, and capable of being isolated by means of a sluice valve. In this box the salt is collected until full, and the communicating valve is then closed and the salt quickly washed and dried by means of vacuum and steam, and is then removed through the door in a clean and comparatively dry state ready for immediate re-use in the soap pans. A somewhat similar salt box has been described on p. 30, under **Foster's Waste Lye Evaporator**.

For the *larger plants*, however, **Scott's Patent Automatic Discharger** is used, which works automatically, continuously discharging moist salt, which is finally dried and washed in a centrifugal machine; only about 0.25 per cent. of glycerine is present.

Fig. 13 shows the arrangement of this machine, while Fig. 12 shows its mode of attachment to the evaporator.

The drum is rotated by means of a rack carried on the outside of the drum, and the centre shaft does nothing but act as a pivot. No power is put through it and so there is no danger of twisting it.



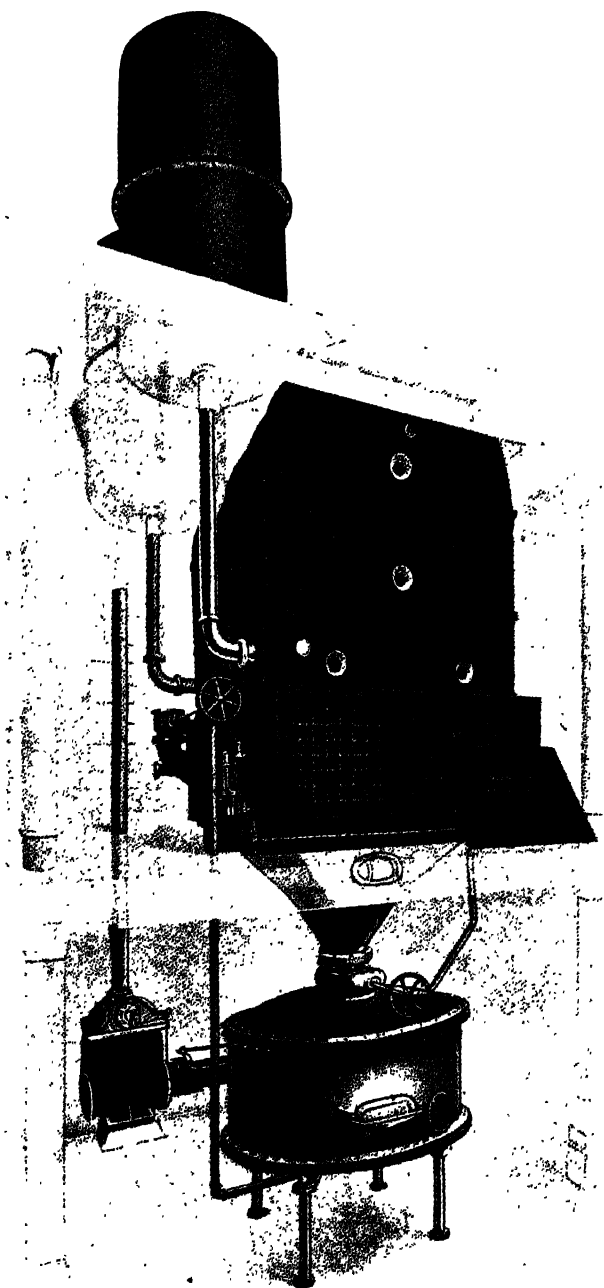


FIG. 15.—Swenson Single Effect for Glycerine.

the springs working over these make up any expansion or contraction, thus ensuring perfect tightness with a minimum of friction, the power required to drive them being exceedingly small. The faces of the moving parts constantly polish one another, and leakage and loss of vacuum are avoided.

The construction is simple and the adjustment can be made by any unskilled man.

These dischargers are made in all metals.

These machines are also supplied with counter attached so as to act as measuring machines.

Fig. 14 shows a general view of a glycerine works fitted with these machines, with mechanical salt extractors and conveying arrangements and centrifugal machine for drying the salt.

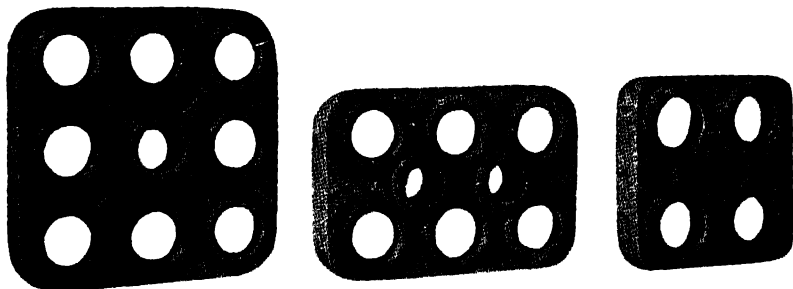


FIG. 16.—Swenson Tube Packing Plates.

These are bolted to the tube sheet and hold the rubber gaskets against the tube sheet and tube.

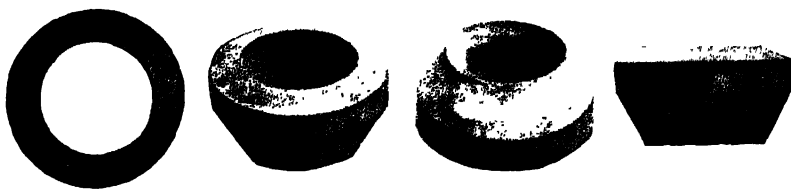


FIG. 17.—Swenson Rubber Tube Gaskets.

For making steam and vacuum tight connection between tube sheets and tubes.

**Swenson's Evaporators for Soap Lye.**—The standard Swenson evaporators differ from the evaporator previously described, in that the evaporator (made of iron) is fitted with *horizontal* brass or copper tubes, the steam circulating *outside* the tubes and the liquor inside. It is stated that these brass tubes do not have to be replaced so often as when iron tubes are used. The construction is obvious from the illustration. The apparatus is a rectangular evaporator with horizontal tubes located near the bottom of each effect. It is made up in sections of heavy cast-iron plates with machined and drilled faces or flanges. The assembled castings are bolted together against suitable packing material (usually sheet asbestos), making a vacuum-tight joint. There is a steam chest at each end cast as an integral part of the vertical tube sheets. Each tube passes well through both tube sheets and is packed in by standard Swenson packing plates and rubber gaskets. This scheme of packing makes possible the use of any material or gauge of tubing the requirements demand, and makes renewal easy. Being completely submerged, the tubes do not burn or scorch the liquor.

The same firm also make evaporators fitted with an internal steam basket

(Fig. 18), the steam entering at the top centre (as in Garnigue's plant) and being distributed around the vertical tubes expanded in top and bottom heads.

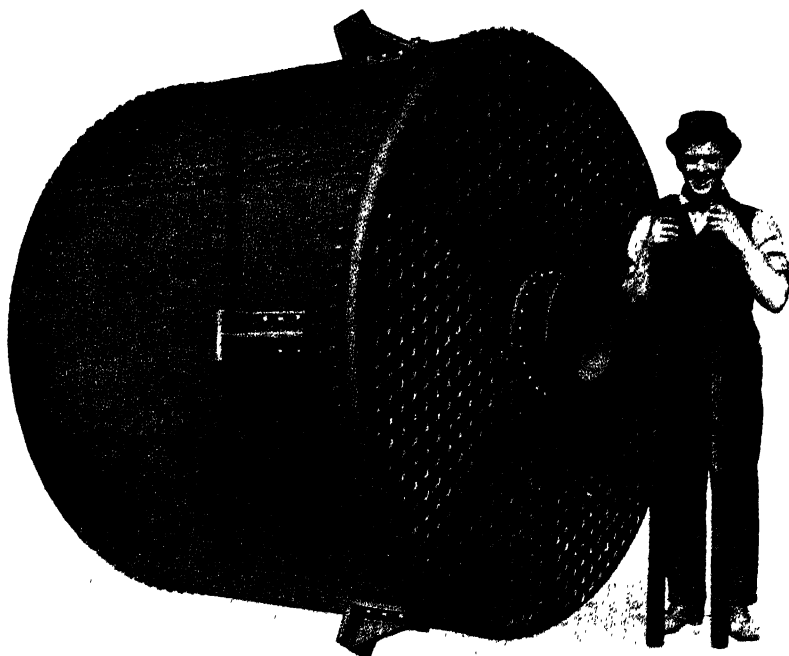


FIG. 18.--Swenson Internal Steam Basket.  
(Fitted in the Swenson Basket-Type Evaporators.)

The uprush of liquor occurs through the narrow annular tubes, and the down-take occurs over the outside of the basket, in the wide annular space left between it and the outside of the evaporator.



## CHAPTER V

SOAP LYE GLYCEROL (*continued*).—CONCENTRATION OF PURIFIED SOAP LYES FOR CRUDE GLYCEROL IN A SINGLE EFFECT PAN EVAPORATOR

THE following descriptions represent current American and English practice such as is practised in most soapworks.<sup>1</sup>

The evaporator used is a single effect with two salt boxes.

The single effect evaporator is less costly in initial outlay, but requires approximately twice as much steam as double effect evaporator doing the same work.

Figs. 19 and 20 show the equipment used in America, and recommended by Wurster and Sanger, of Chicago.

In Fig. 19 A is the evaporator, B<sub>1</sub> and B<sub>2</sub> are the two salt boxes, C is the catch-all, D leads to a jet condenser, while E is the vacuum pump.

Fig. 20 shows the same type of plant, but fitted with a *barometric* condenser F, a column of liquid being held suspended in the tube G against the vacuum created by the pump E.

Fig. 21 shows the layout of a typical English plant made by Messrs Blair, Campbell, & M'Lean, of Glasgow. The drawing is self-explanatory, but the reader should notice the additional salt-draining tank 18 and the drier 19 for salt from the drainer. Notice the type of catch-all 37 and the jet condenser 41 attached to the vacuum pump 30.

Fig. 22 shows a Garrigue's evaporator fitted with a basket-lined catch-all 25, which leads into a barometric condenser 35 attached to the vacuum pump 38.

The evaporator consists of the vapour belt, calandria or steam chest, cover and bottom. It should be equipped with a water-gauge column, thermometer, and vacuum gauge, together with the necessary openings for liquor, steam, and vapour pipe connections.

The vapour belt should be equipped with suitable deflector plates to aid in circulation, and also to aid in the prevention of glycerine losses through entrainment. It should also have sight glass openings so that boiling of the liquor may be observed.

Indicating instruments, such as recording vacuum and temperature gauges, have been brought to a high degree of accuracy, and all glycerol evaporators should be equipped with such instruments.

The recording thermometer has the advantage that the operator may judge the concentration of the liquid by its indications. Any sudden change in vacuum is at once indicated on the thermometer chart as the temperature decreases as the vacuum increases. Suitable water gauges and peep holes are also important, since they indicate the liquid level and the height to which the liquid boils up.

**Calandria.**—The calandria is usually of the standard vertical tube type. A common arrangement is to have copper tubes expanded into copper tube sheets,

<sup>1</sup> W. E. Sanger. *Chem. and Metall. Eng.*, vol. xxvi., June 28, 1922.

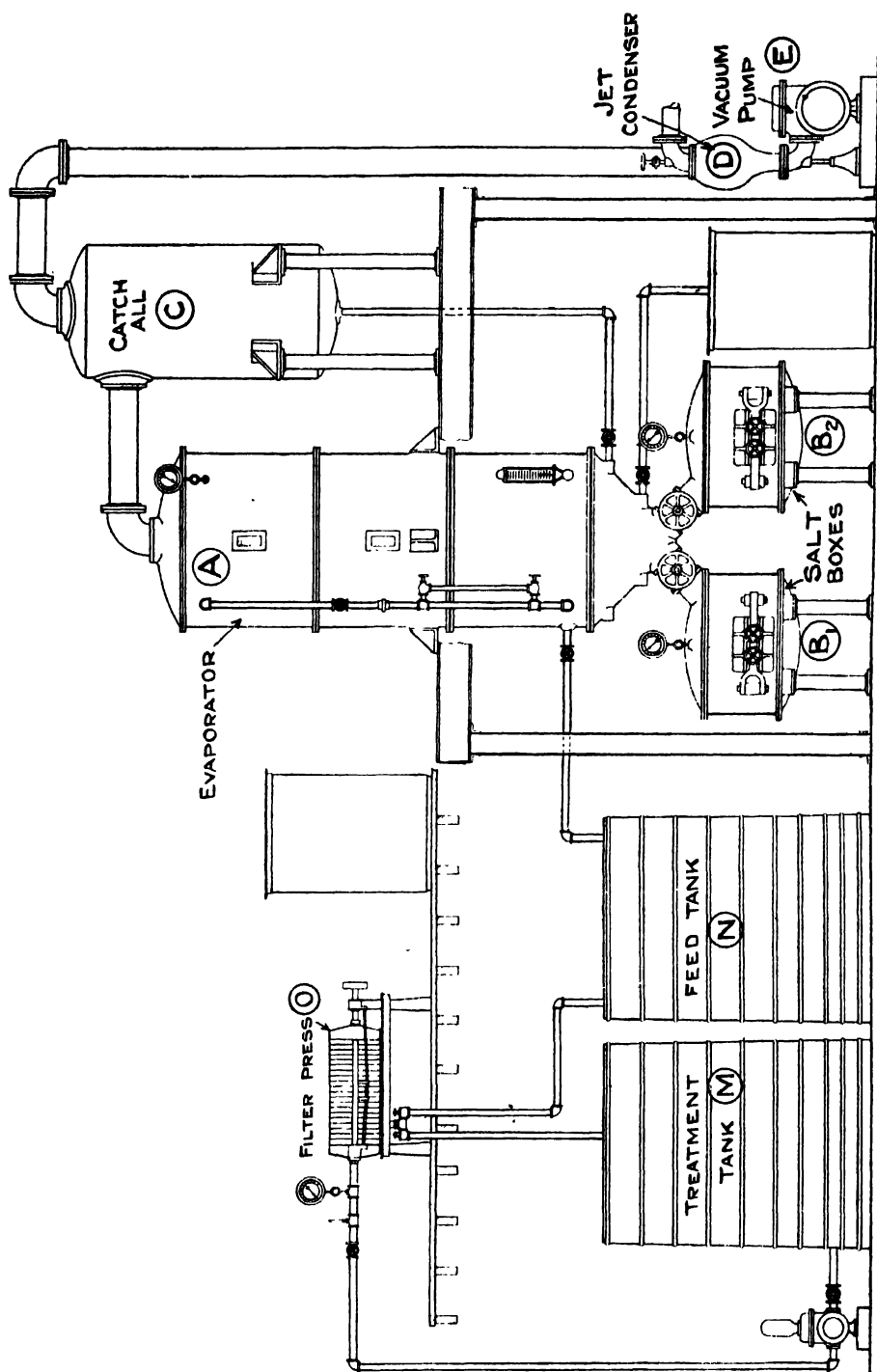


FIG. 19.—American Single Effect Evaporator for Concentrating Soap Lyes, fitted with Barometric Condenser.

the body of the calandria being of cast iron. The calandria should be so designed that there is free and positive circulation of the liquor in order that the tubes will not become salted. It should be equipped with baffle plates to aid the circulation of steam and to sweep out any non-condensable gases. It is further equipped with a steam inlet connection and condensation drain.

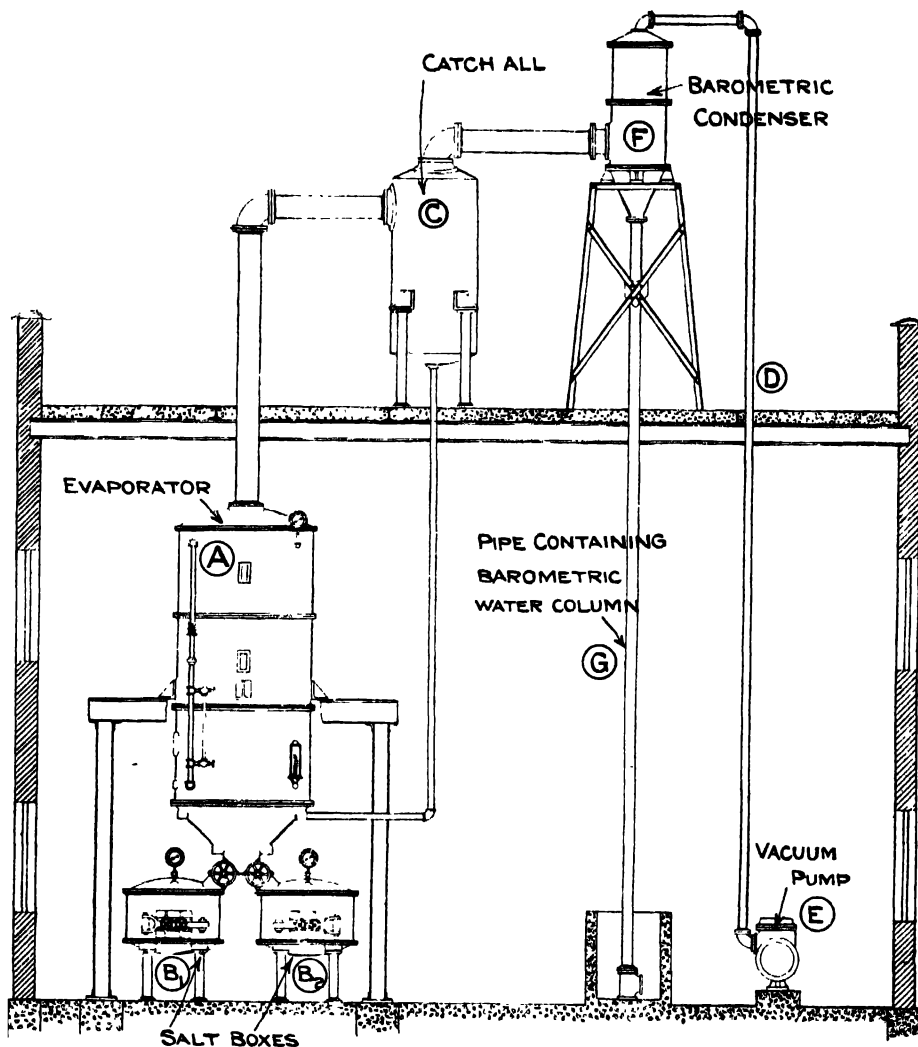


FIG. 20.—American Single Effect Evaporator for Soap Lyes, fitted with Jet Condenser.

The cover may be equipped with a faced flange for vapour pipe connection, or this connection may be taken from the vapour belt.

The bottom should be of the conical type tapped for liquor lines and with openings for drawing off the salt.

**Salt Boxes.**—Salt boxes are used for the purpose of receiving the salt thrown out of solution upon concentration of the spent lye. They are connected to the bottom of the evaporator by means of salt valves, which are usually of the double

wedge gate type. The bottoms of the boxes are connected back into the body of the evaporator above the calandria by means of salt box return lines. These lines should be equipped with valves and fittings so that steam or water may be passed to the salt boxes or to the evaporator.

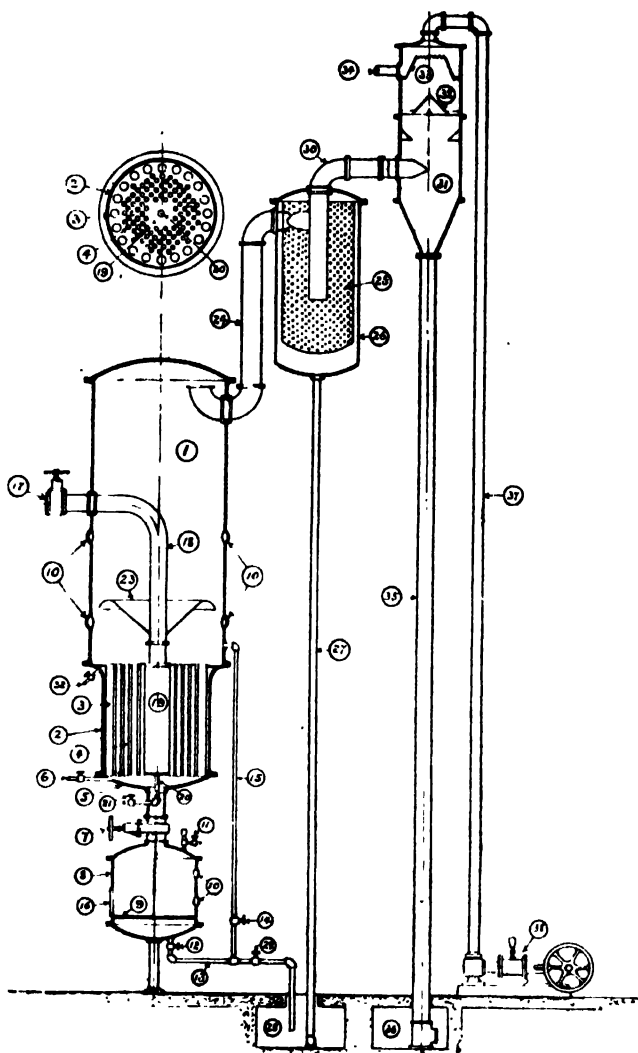


FIG 22.—Garrigue Evaporator, showing Basket Catch-all and Barometric Condenser.

**Catch-Alls.**—A catch-all is used for decreasing losses by entrainment and also as a separator if a charge is pulled over from the evaporator. It should be equipped with a drain line running to the evaporator and also with a water-gauge column.

The most common and least expensive type of catch-all is in the form of a closed cylinder with dished head and bottom.

The vapour inlet is at the side and the outlet at the top, or vice versa. A pipe is fitted inside which extends to about 15 in. below the bottom of the side vapour pipe.

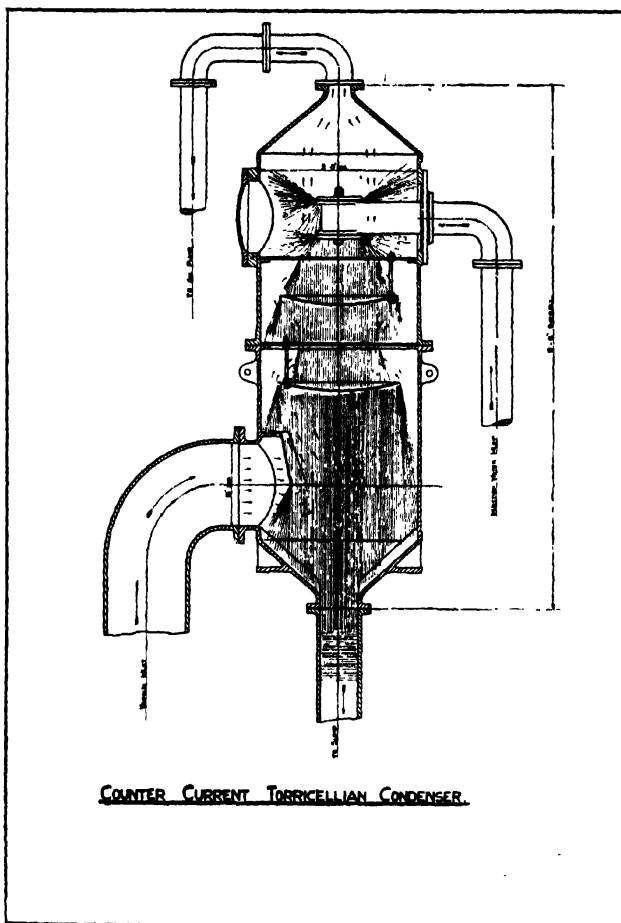




More efficient catch-alls are made like steam separators, having fluted walls or with a cylindrical basket (or inner shell) suspended inside the catch-all, through the walls of which the vapours must pass before leaving the catch-all (see Fig. 22, Garrigue's Evaporators).

The lining plates may be of different shapes; usually the vapours enter the catch-all tangentially, and any entrained liquid is thrown against the curved outer wall of the catch-all by centrifugal force and runs to the bottom, whence it is returned to the evaporator.

The vapours pass through openings in the lining plates and thence pass to the condenser.



COUNTER CURRENT TORRICELLIAN CONDENSER.

FIG. 23.—Counter-Current Torricellian Condenser.

**Condensers.**—The condenser may be of the barometric type or else of the jet type directly connected to the vacuum pump. A barometric condenser serves to maintain a more even vacuum than is obtained with the jet type.

Figs. 23 and 24 show two views of jet condensers. In one the water is simply run down a chamber provided with baffle plates, and in the other the water is sprayed into the chamber as a fine spray so as to increase the condensing surface.

This is a typical English plant manufactured by Messrs Blair, Campbell, & M'Lean Ltd., of Glasgow. It will be noticed that the water is sprayed into the chamber as a fine spray through an adjustable spreader pipe of special design. The baffles over which the water flows are so arranged as to give a maximum time contact between the vapours and the water.

Fig. 22, p. 42 (Garrigue's Evaporator), shows an evaporator fitted with a barometric condenser 35 attached to the vacuum pump 38.

**Operation of a Single Effect Unit.**—In starting the evaporator in operation, the salt valves should be closed, the salt box return lines should be open, and all other lines should be closed. The vacuum pump is started and a small amount of water turned on to the condenser. Under these conditions vacuum is pulled on the whole system.

After the vacuum reaches 15 in. or is sufficiently high to pull lye into the evaporator, it is filled to about one-half the height of the calandria. When the vacuum reaches 23 in. or more, a small amount of steam is turned into the calandria.

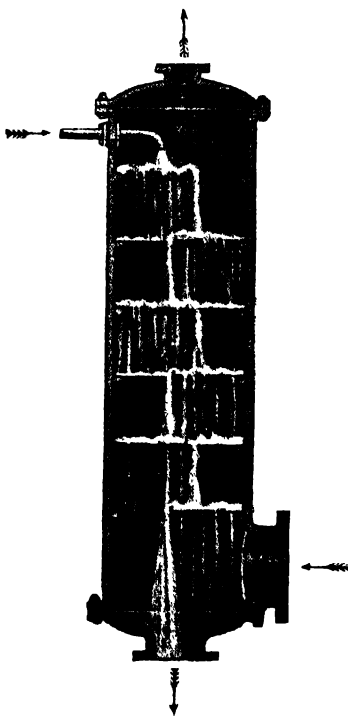


FIG. 24.—Simple Jet Condenser.

Experience soon teaches just how much steam should be turned on. This should be done slowly enough so that boiling of the lye starts when the vacuum reaches about 25 in. Boiling should start slowly enough so that there is a drop in vacuum not to exceed 2 in. If the vacuum falls more than this, there is great danger of loss of liquor when the vacuum again rises, which it does quite rapidly as soon as the vapours reach the condensing water.

As soon as boiling commences, more water is turned into the condenser so that vacuum may be maintained. When the lye begins to boil, more steam is slowly turned into the calandria and more lye is fed to the evaporator to maintain a level about two-thirds of the height of the calandria. When the lye is boiling well the level in the evaporator is raised and the level of the liquor so maintained that the tubes are continually wet. Steam is increased until there is just a positive pressure on the condensation drain from the calandria. Under such conditions the evaporator is doing its normal work.



**Filling the Salt Boxes.**—After a period depending on the salt content of the lye, salt will begin to crystallise out of the liquor and will drop into the bottom of the evaporator. The presence of salt may be detected in the liquor which is thrown against the sight glasses on the vapour belt. After salt begins to form the lye has no further value in dissolving salt remaining on the tubes from a previous run, as it is then a supersaturated salt solution; the salt valve on one salt box is opened, the steam is turned off of the evaporator momentarily, and the charge is dropped into the salt box. The salt valve is left open and the evaporator body is again filled with fresh lye to the former level. While fresh lye is being fed, steam is turned on the calandria, so that the lye is heated to the boiling point as it is fed to the evaporator.

As evaporation continues, the lye again becomes a supersaturated salt solution and salt crystals will fall into the bottom of the evaporator, whence they drop into the salt box. Evaporation is continued, and when the salt box is full the salt valve connecting this box to the evaporator is closed and the valve on the salt box return line is opened. The salt valve on the second salt box is opened and the charge is dropped from the evaporator into the second salt box, as above described.

**Drying and Removing Salt.**—The salt in the first box is now ready for drying. The salt box return line is open, thus connecting the bottom of the box with the body of the evaporator above the calandria. The vacuum breaker, which is a valve at the end of a nipple, is opened. This breaks vacuum or puts atmospheric pressure on the top of the salt and liquor in the salt box, whereas the bottom of the box is under vacuum through being connected into the evaporator which is under vacuum. The liquor mixed with the salt will draw through the salt and pass back into the evaporator body. It can be determined when the liquor is passing through by feeling of the salt return line, which becomes warm, or the level of the liquor may be seen in sight glasses in the salt box.

After the liquor starts to pass off from the salt box, the vacuum breaker is closed and steam is turned on to the top of the salt. Enough steam is kept on to show a very low pressure on the box. After the liquor has all been drawn off into the evaporator body, steam is kept turned on for fifteen to thirty minutes to dry the salt. When the salt is dry, steam is turned off and the valve on the salt box return line is closed. The salt box is now completely separated from the evaporator. The vacuum breaker is opened. The salt door is opened and the salt removed.

When the salt box is empty, the salt door is closed, and the valve on the salt box return line is opened very slowly to pull vacuum on the salt box so that it will be ready for dropping the next charge from the evaporator.

**Concentrating and Finishing.**—The operation of filling and emptying the salt boxes is repeated as often as necessary until the half-crude stage of glycerine is reached. The half-crude stage is readily recognised, because at this time, maintaining the same level in the evaporator and the same amount of steam on the calandria, both the vacuum on the equipment and the pressure on the calandria tend to rise quite markedly. Steam is then gradually reduced until there is about 5 lbs. of pressure on the condensation drain with but little steam turned on the calandria.

With these conditions obtaining and with one salt valve open, the feed to the evaporator is shut off and the charge in the evaporator is concentrated until the liquor has a temperature of about 165° F. under 26 in. of vacuum, or 170° F. under 25 in. of vacuum. The salt valve is closed and the charge in the evaporator is not dropped again. The salt box is steamed as usual and the charge in the evaporator is concentrated until it has a temperature of 200° F. under not less than 27 in. of vacuum.

If the spent lye has been properly treated, this finishing condition will produce a crude glycerine containing in excess of 80 per cent. glycerol. Analyses of the

crude produced should be made from time to time and the finishing temperature decreased if possible, as there is some loss of glycerine when finishing at 200°. Good crude glycerine has been obtained with a finishing temperature of 170° F.

**Advantages of Evaporating under Vacuum.**—Evaporation under vacuum is carried on primarily for the purpose of increasing the rate of evaporation and not for the saving of steam, as will be seen from the following :—

Under atmospheric pressure, saturated steam has a total heat of 1150.4 B.T.U., while under 26.85 in. of vacuum it has a total heat of 1110.6 B.T.U. The difference in total heat is 39.8 B.T.U., or 3.46 per cent. The saving in heat units by evaporating under this vacuum is then 3.46 per cent., but against this saving there are the charges for steam consumed by the vacuum pump and also the condensing water required.

The advantages of evaporating spent lye under vacuum are primarily that to evaporate a given quantity of lye there is a saving in equipment and floor space required and also less loss of glycerine through being able to make crude glycerine at a lower temperature. Also it is possible to use exhaust steam from the pumps and engines.

Rate of evaporation is approximately proportional to the difference in temperature between the heating medium and the medium being heated. Taking, then, the case of evaporating water on which accurate temperature figures are available, assume the steam pressure on the calandria to be 5.3 lbs., at which pressure the temperature of steam is 228° F. Under atmospheric pressure the boiling point of water is 212° F., and under 26.85 in. of vacuum the boiling point of water is 116° F. Boiling under atmospheric pressure, the temperature drop would be 16°, whereas boiling under a vacuum of 26.85 in., the temperature drop would be 112° F. Since the rate of evaporation is roughly proportional to the temperature drop, the rate of evaporation under the above vacuum would be about seven times as great as under atmospheric pressure.

**Necessity for Avoiding Sudden Rise in Vacuum.**—Vacuum decreases the temperature at which a liquid will boil. In the case of water it will boil at a temperature as low as 32° F. under perfect vacuum. This fact makes it very important that no sudden rise in vacuum take place in the evaporator.

If water is boiling in an evaporator under 20.04 in. of vacuum, its temperature is 161° F. If the vacuum is 26.85 in., its boiling point is 116° F. If there is present in the evaporator 2,000 lbs. of water boiling under a vacuum of 20.04 in., the total number of B.T.U. present is 2,000 times 1129.9, or 2,259,800. The total amount of heat present in this amount of water under 26.85 in. of vacuum is 2,000 times 1110.6, or 2,221,200 B.T.U.

If the vacuum is suddenly increased from 20.04-26.85 in., water is present in the evaporator, which water has a boiling point of 116° F., and the temperature of which is 161° F. There is then available the difference between the two total heats, or 38,600 B.T.U., which energy very quickly expends itself in converting some of the water into steam. While the amount of steam generated with this excess of heat is only about 35 lbs., yet this steam has a volume in excess of 6,000 cub. ft., which is generated suddenly throughout the 2,000 lbs. of water and will mechanically carry over most of the water to a point beyond the evaporator. When the above conditions exist, the charge may be seen in the catch-all, or if there is no efficient catch-all, it may be seen in the discharge of the vacuum pump.

In a properly designed evaporator this is probably the most prolific source of glycerine losses. For this reason it is advisable to have all evaporators equipped with a recording gauge (either thermometer or vacuum gauge) so that there may be kept a check on how the evaporator is run for the full period of operation.

**Entrainment Losses of Glycerine.**—Entrainment losses of glycerine usually consist in the passing over of small particles of the solution being evaporated.

These extremely fine drops may pass from the surface of the boiling liquor as such, or may be the result of breaking up of larger drops by impingement or the breaking of bubbles. It can be demonstrated mathematically that comparatively large drops of liquor may be carried away with the vapours from the glycerine evaporator.

It will thus be seen that unavoidable, but slight, losses of glycerine are due to entrainment and to the vapour pressure of glycerine solutions, but that the chief source of loss is through boiling over or "spills" in the evaporator due to sudden increase in vacuum.

The only way to reduce loss by entrainment is by proper design of the vapour belt and by the use of an efficient catch-all.

The loss of glycerine vapour is best avoided by reducing the superheating of the liquid and vapours.

**Causes and Remedies for Decreased Rate of Evaporation.**—Decrease in the rate of evaporation of any given glycerine evaporator is most frequently due to the salting up of the tubes, a condition which depends largely upon the design of the calandria and the salt content of the spent soap lye.

If there is a marked decrease in the rate of evaporation, the manholes should be opened so that the calandria may be inspected. If the calandria is clean, the calandria and condensation drain should be tested under water pressure. If the calandria is salted up, the manholes should be closed and the evaporators filled with water so that the calandria is completely immersed, and this water boiled for about fifteen minutes. It should then be drained into a storage tank so that the glycerine may be recovered. This water should be tested with a hydrometer, and if it has a Baumé gravity higher than  $23^{\circ}$  it may be concluded that it is saturated with salt. A second charge of water should then be boiled and tested. If this second wash water tests less than  $23^{\circ}$  it may be run to waste. The manholes should be opened and the calandria examined to see if it is free from salt.

It often happens that there is a small leakage in the steam valve on the calandria, so that when the evaporator is shut down at night the salt deposit on the calandria is baked very hard on. Under these conditions, boiling with water for a short time will not dissolve all the salt, so that the Baumé test will show the presence of only a small amount of salt in solution while the calandria is still coated. It is good practice to fill the glycerine evaporator with water when it is shut down for any length of time.

The condensation drain of the evaporator should be equipped with a compound gauge (pressure and vacuum), so that any leakage in the calandria may be easily detected. Small pinhole leaks usually can be located only by putting a water pressure test on the calandria.

## CHAPTER VI

SOAP LYE GLYCEROL (*continued*).—DOUBLE EFFECT PAN EVAPORATORS USED FOR CONCENTRATING PURIFIED SOAP LYES FOR GLYCEROL RECOVERY

**Double Effect Evaporators.**—By some firms **multiple effect evaporation** is employed for soap lye evaporation. Two or more evaporators are connected in series in such a way that the vapour generated in evaporating liquid in the first effect is utilised to evaporate the contents of the second. By this means the steam consumption is reduced to nearly half in double effect and in triple effect to about one-third.

Against this saving, however, has to be placed depreciation on plant, increased capital outlay, which rapidly mounts up as the number of vessels employed increase; also the manipulation is more complicated.

As a rule the steam chamber of the first vessel is heated with direct steam or with exhaust steam (supplied from the exhaust steam receiver), into which passes the waste steam of the factory. The purified lye circulating through the heated tubes is made to boil at a lower temperature under the reduced pressure than is possible by heating in the open pans.

The vapour given off by the boiling liquor passes through large pipes into the steam chamber of the second vessel, where its latent heat is utilised in producing evaporation, the pressure being further reduced, as this second vessel is under a greater vacuum than No. 1. Thus we get what is termed a “*double effect*” plant.

The vapours discharged from the second vessel during boiling may be passed through pipes to the steam chamber of the third vessel, when we get a “*triple effect*,” and there being condensed, create a partial vacuum in the second vessel. Sometimes the third vessel is heated by means of live steam.

The vapours issuing from the last vessel of the evaporating plant pass into a condenser where they are condensed by injected water, which is drawn off by means of the pump employed for maintaining a vacuum of 28 in. in the vessel.

In some recent designs (see, for example, Figs. 26, 29) the vapours generated in the last vessel are made to preheat the fresh lye passing to the first evaporator, which latter helps to condense the vapour in its turn. The usual arrangement consists of a number of tubes fixed in a casing, the tubes containing the lye while the vapours pass through the spaces surrounding the tubes.

In some works the *first effect* is used for concentrating the caustic soda liquors (previously made in the works by treating sodium carbonate solution with caustic lime), while the vapours therefrom are passed into the *second effect* and used for concentrating the *soap lye* and removing the salt.

So that a double effect evaporator can be made to handle two different liquors at the same time, thereby securing economy of working and minimum of expense in plant outlay.

Thus the whole object of multiple effects is to utilise all the available heat in performing the greatest amount of work.

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The theory of the plant is explained below in Chapter IX. Special arrangements are made for withdrawing the condensed water from the steam chambers without undue loss of useful heat. Also in order to prevent the glycerol splashing over and being lost by passing into the steam chambers, each plant is fitted with "dash plates," "catch-alls," and "save-alls" of various designs, which will be illustrated below, and which are fitted to each vessel.

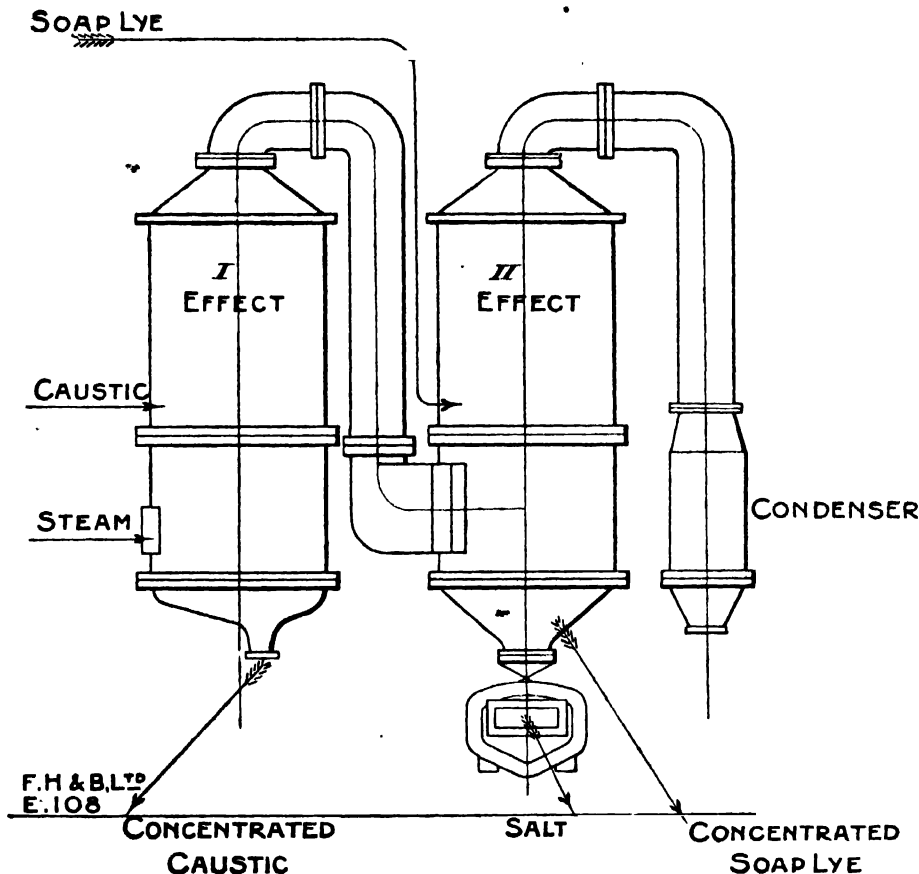


FIG. 25.—Double Effect Evaporator (working on two different liquors).

In the above diagram it is indicated how a vacuum evaporator may be arranged to handle different liquors at the same time, thereby securing economy of working and economy of plant outlay. This system is of very great value, and can be extended to evaporation of as many different liquors as there are vessels in the evaporator plant.

The principle is employed by many soapmakers for the concentration of caustic soda and glycerine simultaneously. Obviously it avoids the use of two smaller but separate installations.

Thus Fig. 26 shows a double effect evaporator by **Manlove, Alliott, & Co., of Nottingham**, England, which is particularly instructive and represents modern practice, the drawing being supplied to the author by Mr Alliott. The following is the explanation of the lettering: AA, first and second vessels; B, preheater; C, jet condenser; D, wet vacuum pump driven by double-acting steam engine; E, salting-out box; F, steam trap for draining calandria of first effect; G, duplex pump draining calandria of second effect.

The fittings on the vessels are as follows:  $a_1$ , drop separator;  $a_2$ , baffle

plate;  $a_3$ , slight and light glasses;  $a_4$ , liquor inlet valve to first vessel;  $a_5$ , boiling tubes in calandria;  $a_6$ , liquor downtake;  $a_7$ , steam inlet;  $a_8$ , inspection manhole and draining cock;  $a_9$ , liquor pipe taking partially concentrated liquor from first to second vessel;  $a_{10}$ , outlet cock for crude glycerine;  $a_{11}$ , sampling apparatus.

The fittings on the salt box are as follows:  $b_1$ , steam inlet;  $b_2$ , sluice valve, with steam cock for preventing blockage;  $b_3$ , filter surface;  $b_4$ , return pipe for filtered liquor.

The method of operation is as follows: The liquor is admitted into the first vessel and is partially concentrated. As evaporation proceeds, quantities are passed over to the second vessel and fresh liquor run in. This goes on until the liquor in the second vessel has been concentrated down to a point where it contains about 80 per cent. of glycerine and registers a density of  $42^\circ$  Tw. ( $25^\circ$  Bé.). This can be judged by use of the sampling apparatus shown and also

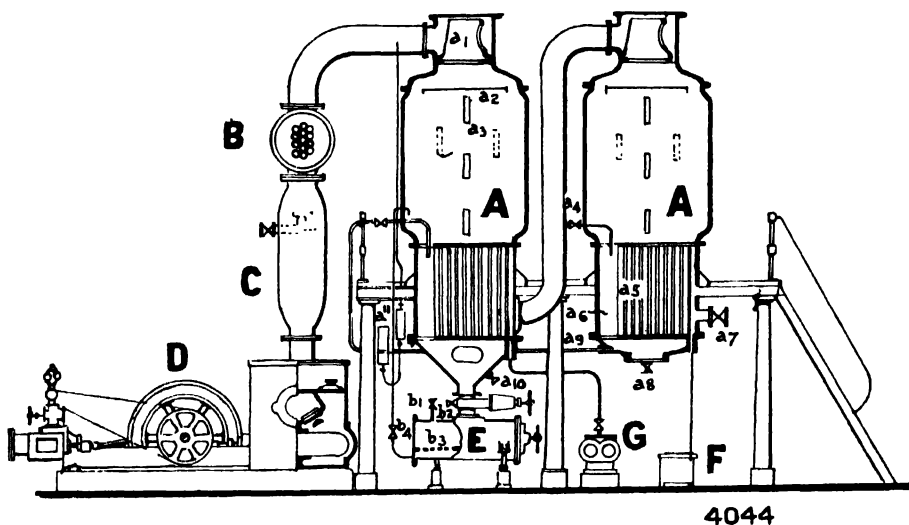


FIG. 26. —Double Effect Evaporator for Soap Lye.

(Diagram Elevation. Messrs Manlove, Alliott, & Co., of Nottingham.)

by inspection of the temperature shown on the thalpotassimeter or special thermometer.

There is one of these thermometers on each vessel though these are not indicated on the diagram.

As concentration proceeds salt begins to be forced out of solution in the second vessel, and this drops out through the sluice valve into the filter box, where it is retained on a specially constructed filter surface.

From time to time the sluice is closed, the return pipe is opened so that there is a direct connection from below this filter surface back into the upper vessel, and the steam cock is then opened so that the salt is steamed and the liquor forced out. The door is then opened and the salt is raked out.

This apparatus is fitted with a tubular preheater B, so that the lye before being fed into the first evaporators is preheated by the hot vapours passing away from the second evaporator; thus the cold entering lye serves to condense the vapour issuing from the second effect and simultaneously is preheated by waste heat before entering the first effect evaporator.

The use of this preheater B has a very beneficial effect both on the capacity of the plant and on the economy. As a portion only of the vapour can be used for

this purpose, an additional condenser *C* (as shown) is necessary. The type of vacuum pump indicated is a very good one as, should there be any foam over, it immediately shows at the top of the pump and gives warning to the attendant.

Instead of having a separate pump for the calandria of the second vessel, this is often arranged as an auxiliary on the side of the vacuum pump, and is then of the same type.

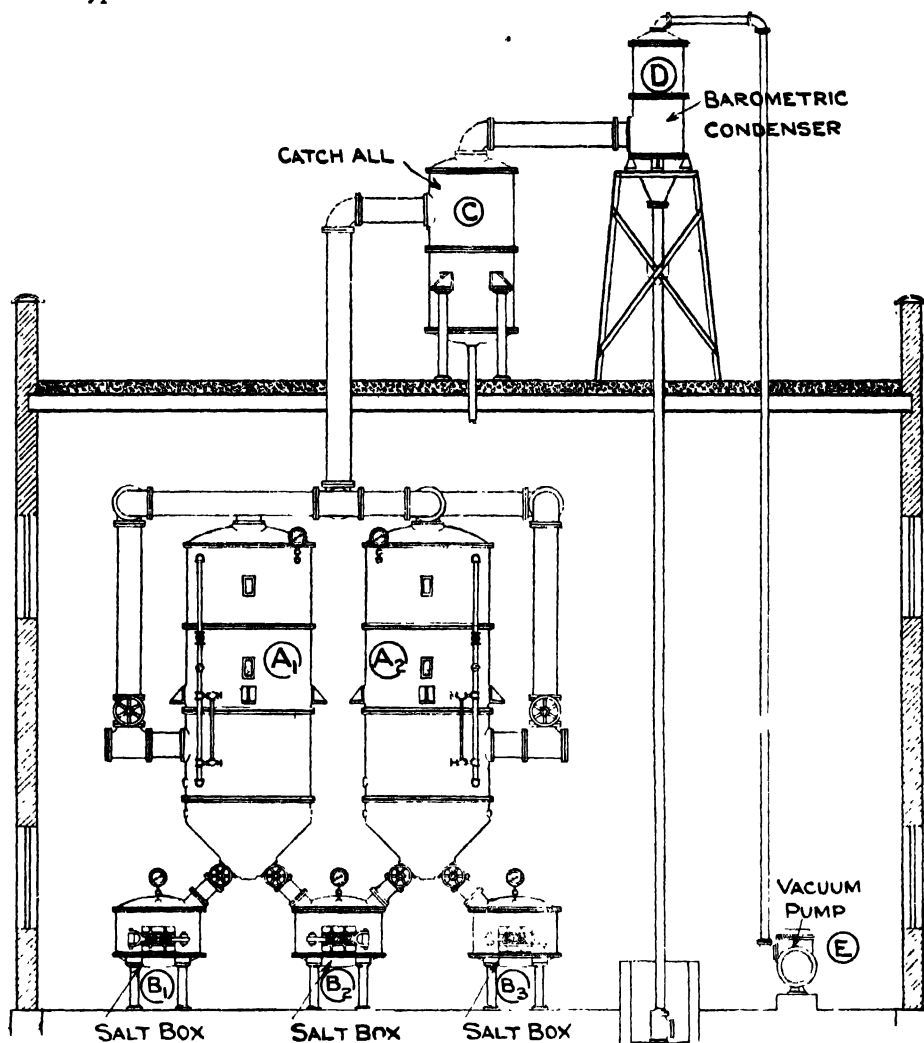


FIG. 27.—Sanger's Double Effect Soap Lye Concentration Plant, using Barometric Condenser.

Foaming is generally due to faulty treatment of the soap lye and occurs very suddenly. It can be dealt with by any form of baffle or drop separator.

In the top of the pan baffle plates and drop separators are shown, and the purpose of this is to catch any drops of liquor that would otherwise be carried over, quite apart from any question of foaming.

The vessels are also of a good height, which in itself is one of the best protections against entrainment losses. The best designs of evaporator for this purpose have









comparatively short tubes, say 4 ft. long, with the liquor downtake at the side. This gives an even and satisfactory boiling.

Fig. 27 shows an arrangement of double effect plant for soap lye concentrated advocated by Sanger.<sup>1</sup>

It will be seen that a barometric condenser is employed instead of jet or tubular condensers, and that three salt boxes go to every two effects.

Some plants give difficulty because the tubes become blocked up with deposited salt, thereby diminishing and retarding evaporation. In this case the salt must be dissolved with lyes or water. However, with careful working the difficulty is obviated by washing out with weak lyes after each batch of crude glycerol has been run away. Another method is to increase the circulation, so that the liquor rushing up the pipes carries away the salt.

*Lewkowitsch* (see his "Chemical Technology of Oils, Fats, and Waxes," 5th edition, vol. iii., p. 368; also *Jour. Soc. Chem. Ind.*, 1905, 1149, English Patents, 28,747, 1897; 30,616, 1897; 14,750, 1909) claims that by the use of a revolving heater the salting up of the tubes is prevented. His plant, however, does not seem to have become established extensively in the industry.

**Messrs Blair, Campbell, & M'Lean's** (Glasgow) double effect evaporator is shown in Fig. 28. A dry vacuum pump 50 is employed to produce the vacuum combined with a barometric condenser 45. The vapour arising from the second evaporator first passes through a "save-all" 42, where any entrained liquid is caught and runs back through the pipe 41 into the evaporator. The uncondensed vapour passes through the vertical pipe 44 to the torricellian or barometric condenser 45, where it meets with a stream of cold water. Occasionally the ascending vapours are condensed by lye—their heat being utilised to heat the lye before it passes into the evaporator.

The dotted lines show the arrangements adopted in the latter case. The torricellian condenser consists in a sense of a barometer, in the upper part of which the condensation of the vapours takes place in the presence of inrunning cold water. The exit tube 48 leading away the condensed water must be at least 32 ft. above the level of the ground, in order that the water column contained therein should sustain the atmospheric weight.

The condensing water and the condensed vapours mingle and flow down in a column through the return pipe 48 into an open concrete sealing tank. Meanwhile the dry vacuum pump 50 exhausts air from the system by means of the pipe 49. In some plants a catch-all is fixed at the top of 49, which catches any condensed vapour and allows it to flow back into the water pipe 48 and then into the sealing tank, as in Garrigue's plant (described below).

The removal of non-condensable gases from the steam is an important feature which is attained by drawing off these gases through pipe lines containing valves.

Fig. 29 shows another type of crude glycerine recovery plant with a double effect evaporator manufactured by the same firm.

Instead of using a barometric condenser, however, a tubular surface condenser *w* is used, which is connected with a steam-driven vacuum pump *x*. Also a tubular preheater *F* is fitted to the condenser tube which preheats the lye which is fed into the first effect evaporator.

The drawing is self-explanatory.

**Garrigue's Double Effect Evaporator.**—Figs. 22 and 30 show the arrangement favoured by William Garrigue & Co., of Chicago, U.S.A., for evaporating glycerine. In this apparatus also the vacuum is produced by a dry air pump 38, working in conjunction with a barometric condenser 31 and a catch-all 25 and 26 of special construction.

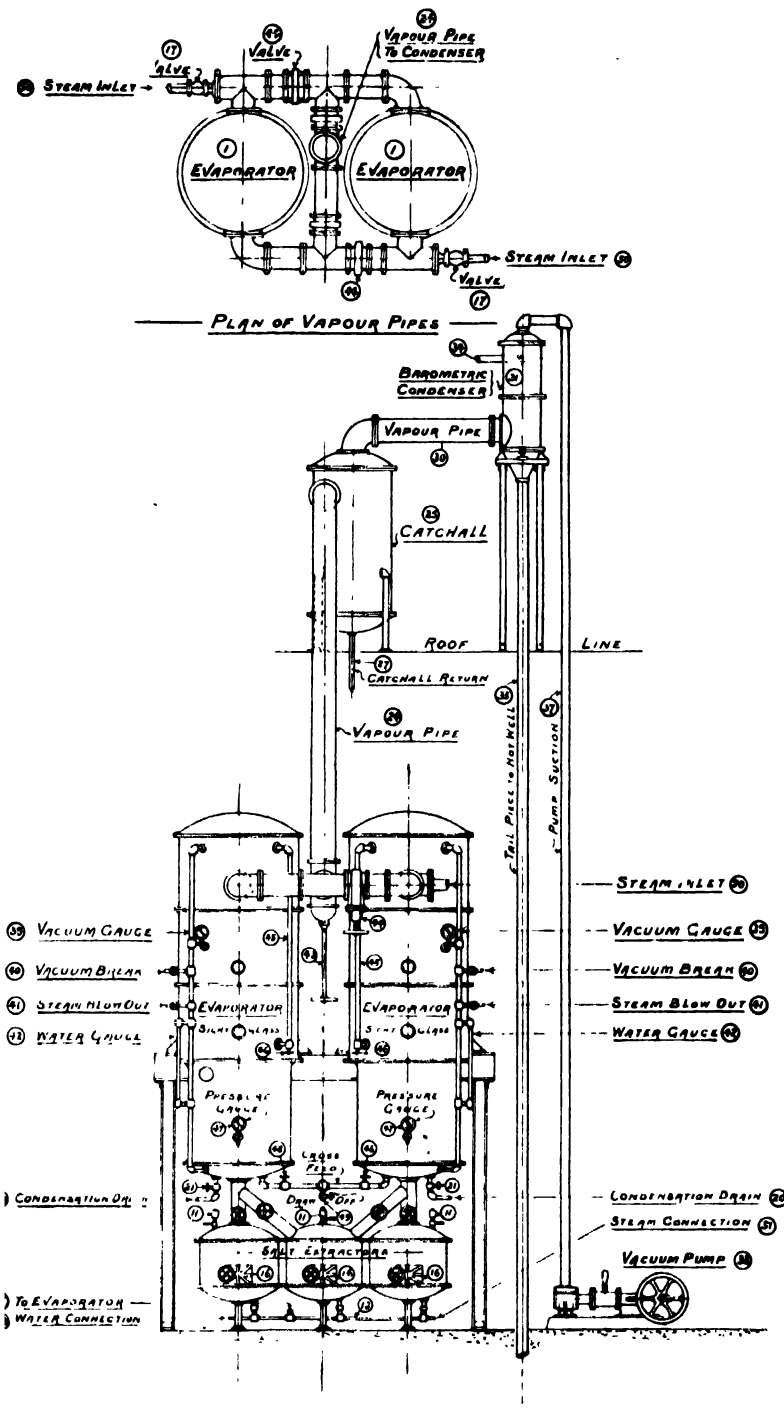


FIG. 30.—Garrigue's Reversible Double Effect Evaporator for Soap Lye Glycerol.



and in which the excess liquid can be held out until the proper conditions are re-established in the evaporator."

"The best insurance against frothing is keeping down the volume of the boiling liquid and keeping it in rapid circulation."

"The best insurance against entrainment is to dash the escaping bubbles against an obstruction and to allow ample height to the outlet."

The vapour from the first effect (not shown in Fig. 22 on p. 42) enters through the pipe 17 and 18 (Fig. 30) in the centre of the heating chest or calandria 19 around the small boiling tubes, and baffle it so that it effectually comes in contact with all the heating surface. The condensed water passes away through the pipe 20 and 21 to a small exit force pump. The calandria is vented at the outside or coolest part, where there is a row of larger tubes 3 for downward circulation of the liquor. Thus the direction of the boiling liquor in the evaporator is from the middle to the sides, from the smaller to a larger area, from a hotter to a colder zone, and the combined area of the downcoming tubes 3 is relatively large in cross section and entirely out of the way of the narrower upward gushing tubes 4, all of which makes for a vigorous circulation. The current of liquid at the bottom of the evaporator is *inward* and sweeps out deposited salts towards the centre, thus allowing the use of a dished bottom 5 instead of a cone, thus minimising the liquid in the machine. The vapour space 1 is made wider than the calandria 2 to allow room for the waves of liquid from the centre to flatten out and also to make an expansion diaphragm of the upper tube sheet to prevent leakage at the tube ends from expansion strains.

In order to prevent entrainment there is a conical dash plate 23 carried on the steam inlet pipe 18, the outward edge of which is curved down so that any liquid thrown against it is projected on to the downcoming tubes 3 of the calandria. The bottom of the salt extractor 8 has a fine screen on which the salt rests. When the salt extractor is filled (as seen through the sight glass 16), the salt valve 7 is closed and the adhering liquid blown from the salt with steam let into the top of the extractor by means of the pipe 11, this liquid returning to the evaporator via the pipe 13, 14, and 15. The salt is also washed.

The larger machines have two salt extractors, one of which is always open.

The reversible double effect plant (Fig. 30) has three extractors, the central one connected to both evaporators. As salt separates only in the second effect, this arrangement allows two extractors for that effect.

**Swenson's Arrangement for Double Effect.**—The arrangement of the plant is illustrated in Fig. 31. Two evaporators are connected for working in double effect for eliminating the bulk of the salt, the partially concentrated glycerol liquor (containing about 50 per cent. glycerol) being then run off from the second effect, and concentrated to 80 per cent. glycerol in a third finishing single effect evaporator seen on the right in Fig. 31.

The advantage of using a "reversible double effect" evaporator is that this gets over the difficulty experienced with the tubes becoming choked with salt, thereby diminishing and retarding evaporation. When this occurs by reversing, *i.e.*, placing the weak lye in the second effect, the salt dissolves and is washed off the tubes.

## CHAPTER VII

SOAP LYE GLYCEROL (*continued*).—PROCESS OF CONCENTRATION OF PURIFIED SOAP LYES FOR CRUDE GLYCERINE IN A DOUBLE EFFECT PAN EVAPORATOR

**Operating a Double Effect Evaporator.**<sup>1</sup>—In starting the evaporator, the valves are set so as to cause the steam to enter the calandria of the first effect, and the vapours from the first effect will pass into the calandria of the second effect.

The condensation drain from the first effect is connected to a steam trap; the condensation drain from the second effect is connected to both a service pump and to a steam trap. The calandria of the second effect is vented near the top into the vapour belt of the second effect to take care of non-condensable vapours which accumulate in this part of the calandria. The vapour line from the second effect is connected to the catch-all, thence to the condenser and vacuum pump.

When starting operation with the double effect evaporator, vacuum is pulled on both of the evaporators until they are under a vacuum of 15 in. Fresh liquid is drawn into both evaporators to a height about one-third of the height of the calandria. When the vacuum reaches about 23 in., steam is slowly turned into the calandria of the first effect. When the liquid in the first effect begins to boil, the vacuum on the first effect will drop. The vapours pass from the vapour belt of the first effect into the calandria of the second effect, where they are condensed and are withdrawn through the service pump. As the vapours are condensed the vacuum again rises, but the starting of the evaporators should be done sufficiently slowly that there will be the minimum drop and subsequent rise in vacuum.

When the liquid boils in the first effect, more steam is turned on until there is just a positive pressure on the condensation drain. Under these conditions the evaporator unit is operating at normal capacity and there will be a difference in vacuum between the two effects of about 10 in. When the liquid in the second effect begins to boil, more liquid is fed from the first effect into the second effect and also from the feed tank to the first effect so as to maintain practically constant levels. As concentration increases in the second effect, it also increases in the first effect and the vacuum difference between the two effects becomes greater. When the stage of "half-crude" glycerine is reached in the second effect the rate of evaporation decreases markedly. The pressure on the calandria of the first effect increases and the vacuum on the first effect decreases; the vacuum on the second effect increases. When the liquid reaches the "half-crude" stage of concentration, steam is shut off from the calandria of the first effect; the vapour line from the first effect to the calandria of the second effect is shut off and the condensation drain from the second effect is connected to the trap. Live steam is then turned on to the calandria of the second effect. The liquid in the first effect is gradually fed into the second effect and any partly concentrated liquid from a previous evaporation

<sup>1</sup> See *W. E. Sanger. Chem. and Metall. Eng.*, vol. xxix., No. 11, September 10, 1923.

is drawn into the second effect. After a short further period of concentration, the pressure on the calandria of the second effect (which is now being run as a single effect evaporator) rises and is maintained at a pressure not exceeding 15 lbs. When the temperature of the concentrated glycerine reaches 170° F. under a vacuum of 27.5 in. or more, the saponification crude should analyse in excess of 88 per cent. glycerol.

Regularly, the temperature of the liquid in a glycerine evaporator is in excess of the temperature necessary to induce boiling as indicated by ebullition. The degree of superheat increases quite regularly after the concentration of the glycerine has reached 50 per cent. glycerol. In tests which the writer has made under normal operating conditions, this degree of superheat amounted to 10° F. in the case of 50 per cent. glycerol solution and to 32° F. in 80 per cent. glycerol solution. These figures were influenced by the fact that the solution came in contact with the thermometer bulb. Making the same observations on the vapour line between the catch-all and the condenser, it was found that the superheat exceeded 30° F.

When the concentration of the glycerine solution exceeds 50 per cent., it is possible to superheat the solution very quickly by suddenly increasing the pressure of the steam on the calandria. In order to induce evaporation it is necessary that the calandria tubes be at a higher temperature than the boiling point of the glycerine solution. Under these conditions the liquid itself becomes superheated, some vapours come in contact with the tubes, and the vapours are further superheated by coming in contact with the particles of liquid which, as already pointed out, are themselves superheated.

**Disastrous Rise in Vacuum.**—While the sources of glycerine loss just mentioned are appreciable, they are a minor item as compared with the losses due to sudden rise in vacuum. There are two periods during the process of evaporation when this condition is likely to obtain. The first is when the evaporator is started in operation and the second when the water supply to the condenser suddenly stops and then suddenly starts.

When starting an evaporator in operation, the vapours generated in the evaporator tend to reduce the vacuum to a degree depending upon the rate at which these are generated.

The vacuum will fall until the vapours come in contact with the water in the condenser, at which time the vacuum will rise suddenly.

By turning steam into the calandria when the vacuum is 25 in., it is possible to heat the liquid so rapidly that the vacuum will be reduced to 15 in. or less before the vapours come into contact with the water in the condenser. When the vapours mix with the water, there is a sudden rise in vacuum which may cause the complete charge in the evaporator to be pulled beyond the catch-all into the condenser where it is lost.

Any glycerine which is lost during evaporation must pass from the evaporator through the vapour pipe and thence to the condenser, when the condensation drain is not inside of the evaporator. Evaporating spent soap lye, the condensing water may be tested for NaCl. The usual procedure in this matter is to have a bleeder on the condenser water line, thus obtaining a continuous sample of the water for the entire period of evaporation. This proves satisfactory where an evaporator is improperly designed and so has a continuous entrainment loss. However, there is usually required an excess of 20 lbs. of water per pound of steam condensed, and where the loss is occasioned by infrequent boiling over of the evaporator, this method of determining glycerol losses is unsatisfactory.

**Detecting Losses with the Tell-Tale.**—A more satisfactory method of detecting loss is by use of "tell-tales."

A "tell-tale" is a small pipe which is inserted inside of the vapour line, being in the form of a half-circle for that portion which is inside of the vapour pipe, the remainder being of full pipe size and screwed into the bottom of the vapour pipe.



The half-circle should project below the lower edge of the vapour pipe so as to catch any condensed liquid in the bottom of the vapour pipe. It should be so placed that the concave surface faces the direction from which the vapours are flowing. The lower end of the tell-tale should be equipped with a valve at a convenient distance from the floor; between this valve and the floor there should be a water gauge column for collecting the sample, which should be removed at frequent intervals. If the lower part of the half-circle is above the bottom of the vapour pipe, probably no samples will be obtained, as the vapours impinging against the baffle will be broken up and carried along with the vapours, which travel at a considerably higher velocity than the vapours in the body of the evaporator. The vapour pipe acts as an air-cooled condenser and will first condense those vapours highest in glycerine. The results of analyses of tell-tales are therefore relative and not absolute.

The vapours condensed in the vapour pipe will collect on the bottom and be carried along in the direction of the flow of vapours.

If the lower end of the half-circle is below the bottom of the inside of the vapour pipe, tell-tales will be obtained.

In the evaporation of sweet water these tell-tales may be analysed for glycerine; in the evaporation of spent soap lyes they may be analysed for both glycerine and salt. In the case of soap lye evaporation, the relation between the salt and glycerine contents of the tell-tales is an indication of the source of glycerine loss. The following table will show the results of a cycle of the production of crude glycerine from spent soap lyes, the tell-tale having been placed between the catch-all and the condenser:—

Time.	Temperature F.	Per Cent. of NaCl.	Per Cent. of Glycerol.	Time.	Temperature F.	Per Cent. of NaCl.	Per Cent. of Glycerol.
A. M.				P. M.			
11.45	157.5	0.35	0.52	2.15	166.5	0.06	0.40
12.0	147.5	0.06	0.50	2.30	167.0	0.06	0.30
P. M.				2.45	167.8	0.03	0.35
12.15	151.0	0.06	0.30	3.0	167.8	0.03	0.50
12.30	152.0	0.06	0.25	3.15	173.1	0.06	0.90
12.45	153.0	0.06	0.25	3.30	174.4	0.06	1.15
1.0	154.0	0.06	0.25	3.45	174.4	0.06	1.00
1.15	155.0	0.06	0.20	4.0	178.2	0.06	1.25
1.30	156.8	0.06	0.25	4.15	185.4	0.06	1.79
1.45	158.0	0.06	0.25	4.30	198.5	0.06	1.89
2.0	161.8	0.06	0.35	4.45	200.0	0.06	2.49

In this table it will be noted that the first tell-tale analysed high in both salt and glycerol. This is accounted for by the fact that steam was turned on the evaporator when the vacuum was 25.4 in.; before the vapours reached the condenser the vacuum had dropped to 22.3 in. and then suddenly rose to 25 in., thus pulling over some of the spent lye from the evaporator into the condenser, where it was lost. A vacuum of approximately 25 in. was maintained throughout the main part of the run, the finish being made under a vacuum of 27.6 in. and a temperature of 200° F.

It is to be particularly noted that after the temperature reached 170° F. the salt content remained constant, while the glycerol content increased from 0.50-2.49 per cent. This shows the tendency of glycerol to distil over with the evaporator vapours at a temperature in excess of 170° F. Crude glycerine should be finished under temperature conditions as low as possible.

**Circulating a Minimum of Water.**—The safest course to pursue in the evaporation of glycerine liquids is to circulate the condensing water, which should

be analysed at frequent intervals. In order that this precaution may be of value, there should be in circulation only the minimum amount of water that will answer the purpose. This is due to the fact that if a large volume of water is in circulation, the dilution of the glycerine lost from the evaporator will be so great that the cost of glycerine recovery would exceed the value of the glycerine. Where the cost of fresh water is sufficiently high, it is economical to use circulating water.

The amount of condensing water required for evaporation increases very rapidly with increase of vacuum. The temperature of condensing water decreases as the vacuum increases. For purposes of illustration, we can assume that in the evaporation of water the temperature of the water after condensation is 5° F. lower than the temperature of steam corresponding to the vacuum; that the barometer is 29.92 in., and that evaporation is carried on under a vacuum of 23.41 in., 26.08 in., and 28 in.; the temperatures for these vacuums are taken from Marks and Davis' Steam Tables.

The temperature of steam at 23.41 in. of vacuum is 144° F. The temperature of the water after condensation will be 139° F. The temperature of steam at 26.08 in. of vacuum is 124° F. and the temperature of the water after condensation will be 119° F. The temperature of steam at 28 in. of vacuum is 100° F. and the temperature of the water condensation will be 95° F. Assume, further, that the temperature of the water entering the condenser is 70° F.

**Calculating Quantity of Condensing Water.**—Kent gives the following formula for determining the quantity of condensing water required in evaporation under vacuum :—

$$Q = \frac{1114 + 0.3T_1 - T_2}{T_2 - T_0},$$

wherein  $T_1$  is the temperature of steam at the exhaust pressure ;

$T_0$  is the temperature of the cooling water entering the condenser ;

$T_2$  is the temperature of the water after condensation ;

$Q$  is the number of pounds of cooling water required per pound of steam condensed.

Evaporating under 23.41 in. of vacuum, as above outlined,

$$Q = \frac{1114 + 0.3(144) - 139}{139 - 70} = 14.8 \text{ lbs. of water per pound of steam condensed.}$$

Evaporating under 26.08 in. of vacuum, as above, outlined.

$$Q = \frac{1114 + 0.3(124) - 119}{119 - 70} = 21 \text{ lbs. of water per pound of steam condensed.}$$

Evaporating under 28 in. of vacuum, as above outlined,

$$Q = \frac{1114 + 0.3(100) - 95}{95 - 70} = 42 \text{ lbs. of water per pound of steam condensed.}$$

*Messrs Lever Brothers and Edwards* propose the following method of procedure if extracting the glycerol from the salt (English Patent, 14,750, 23rd June 1909).—The soap lye, etc., is concentrated in an evaporator containing two or more chambers, and the mother liquor from the first of these is made to pass through the precipitated salt which has been discharged from the second chamber and thence into the second chamber. As it is already practically saturated with salt it will not dissolve any more, but will extract the glycerine which is adherent to the salt discharge from the second chamber. The same process may be repeated with the succeeding chambers when present, whilst the crude glycerine from the last evaporating chamber may be made to pass through the salt which has been discharged from that chamber, so that simultaneously it leaves behind any salt it carries and washes any adherent glycerine from the discharged salt.

**Sause's Apparatus for Concentrating Soap Lyes** (French Patent, 330,140, 11th March 1903).—The apparatus comprises two concentric cylindrical vessels, the outer of which is fixed horizontally on pillars and contains the liquid to be evaporated. The inner vessel, which is heated internally by steam, evaporates the liquid, and being kept in rotation and completely immersed, does not become encrusted by the salt which crystallises out. This salt falls into hoppers in the lower side of the outer vessel and is withdrawn at intervals. The steam formed by evaporation is aspirated from the top of the vessel, and may be passed into the inner cylinder of another similar apparatus.

## CHAPTER VIII

EVAPORATION IN TRIPLE EVAPORATORS—  
THEORY OF MULTIPLE EFFECT EVAP-  
ORATION

**Triple Evaporators: Theory of Multiple Effect.**—Some firms use triple evaporators, thereby effecting a further economy of steam. Fig. 32 shows a Scott triple effect evaporator with a single finisher; a barometric condenser is



FIG. 32.—Scott's Triple Effect Evaporator with Single Finisher.

employed as shown. Fig. 33 shows a section through a triple evaporator plant made by Fullerton, Hodgart, & Barclay Ltd., of Paisley, Scotland.

Fig. 34 shows a sectional view of a **Kestner Patent Climbing Film Evaporator** working in triple effect. This latter illustration is of particular interest, as it shows clearly the various changes that occur in the transfer of steam,





vapours, and liquors at different temperatures in their stages through a triple effect. The diagram is based on an evaporation of 75 per cent. by weight of the liquor dealt with; thus, 4 tons of liquor enter the first effect of the evaporator and 1 ton of steam, and there leaves the last effect 1 ton of vapour which goes to the condenser, 1 ton of concentrated liquor, and 3 tons of condensed steam and vapour.

Reavell ("Evaporation in the Chemical Industry," *Jour. Soc. Chem. Ind.*, 1918, 37, 175 T.) makes the following remarks on the subject:—

"The principle of multiple effect evaporation is that by alternate evaporation

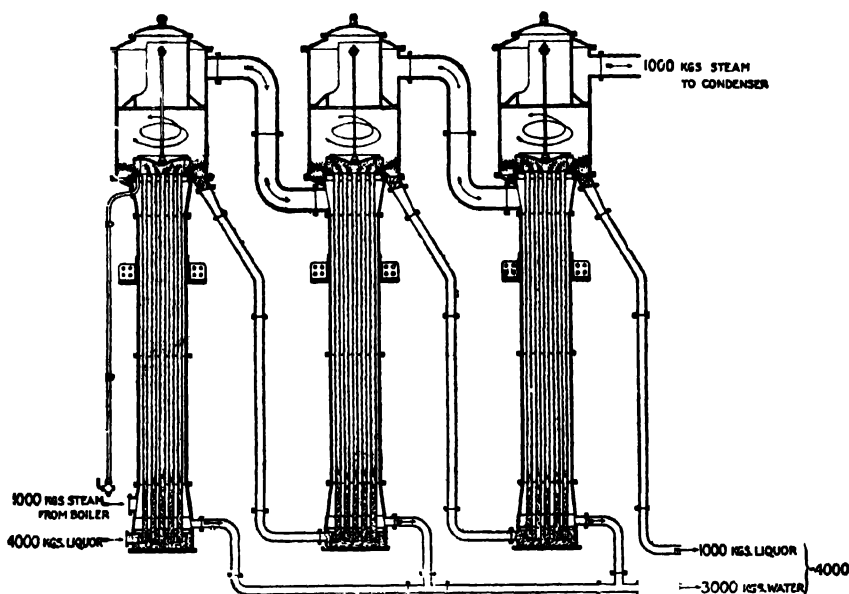


FIG. 34.—Kestner Patent Climbing Film Evaporator Working in Triple Effect.

and condensation the latent heat is exchanged successively, as a means of separating water from solids."

"Thus (see Fig. 34) if 1 kilo of steam be condensed in the first calandria of a triple effect through which liquor is passing, 1 kilo of condensed water would be produced from the liquor in each of the calandrias of Nos. 2 and 3."

"If, therefore, an operation commences with 1 kilo of boiler steam and 3 kilos of water to be evaporated, then 3 kilos of condensed water are recovered and 1 kilo of steam at a lower temperature and pressure than that of the live steam supplied to the first effect."

"The cycle of operation finishes by producing 3 kilos of condensed water and 1 kilo of vapour at a low temperature and pressure, thus showing that what has happened is merely a transfer of heat."

**Economy Rating of Evaporators.**—The following data is supplied by the Swenson Evaporator Co., of Chicago, U.S.A. :—

**STEAM CONSUMPTION OF EVAPORATORS AND COOLING WATER  
REQUIREMENTS OF CONDENSERS**

1 Total Evaporation in U.S. Gal. per Hour.	2 Steam Consumed, Lbs. per Hour.				3 Cooling Water to Condenser—U.S. Gallons per Minute.											
	Single Effect.	Double Effect.	Triple Effect.	Quad-ruple Effect.	Single Effect.			Double Effect.			Triple Effect.			Quadruple Effect.		
					Temperature of Injection—° F.			Temperature of Injection—° F.			Temperature of Injection—° F.			Temperature of Injection—° F.		
					60	70	80	60	70	80	60	70	80	60	70	80
100	925	465	310	230	42	52	70	21	26	35	17	23	11	13	18	
150	1,390	695	465	345	63	78	105	32	39	53	21	26	16	20	26	
200	1,850	925	620	465	84	104	140	42	52	70	28	35	21	26	35	
300	2,775	1,390	925	695	126	156	210	63	78	105	42	52	32	39	53	
400	3,700	1,850	1,230	925	168	208	280	84	104	140	56	69	42	52	70	
500	4,625	2,315	1,540	1,160	210	260	350	105	130	175	70	87	53	65	88	
750	6,940	3,475	2,315	1,730	290	360	480	160	195	265	105	130	79	98	130	
1,000	9,250	4,630	3,080	2,310	390	480	640	210	260	350	140	175	105	130	175	
1,250	11,560	5,780	3,860	2,890	490	600	800	245	300	400	175	215	130	165	220	
1,500	13,880	6,940	4,630	3,470	585	720	960	295	360	480	210	260	160	195	265	
2,000	18,500	9,250	6,170	4,630	780	960	1280	390	480	640	260	320	210	260	350	
2,500	23,130	11,570	7,710	5,790	975	1200	1600	490	600	800	325	400	245	300	400	
3,000	27,750	13,880	9,250	6,940	1170	1440	1920	585	720	960	390	480	295	360	480	
4,000	37,000	18,500	12,340	9,250	1560	1920	2560	780	960	1280	520	640	390	480	640	
5,000	46,250	23,130	15,400	11,560	1950	2400	3200	975	1200	1600	650	800	490	600	800	
6,000	55,500	27,750	18,500	13,880	2340	2880	3840	1170	1440	1920	780	960	585	720	960	
7,000	64,750	32,380	21,580	16,190	2730	3360	4480	1365	1680	2240	910	1120	685	840	1120	
8,000	74,000	37,000	24,670	18,500	3120	3840	5120	1560	1920	2560	1040	1280	780	960	1280	
9,000	83,250	41,630	27,750	20,810	3510	4320	5760	1505	2160	2880	1170	1440	880	1080	1440	
10,000	92,500	46,250	30,840	23,130	3900	4800	6400	1950	2400	3200	1300	1600	975	1200	1600	
12,000	111,000	55,500	37,000	27,750	4680	5760	7680	2340	2880	3840	1560	1920	1170	1440	1920	

One U.S. gallon = 1.2 British Imperial gallon.

Figures in this table do not represent the best performances of evaporators and condensers, but are compiled with reasonable allowance for the fluctuations and variations of average practice. Steam and cooling water requirements will often be found less, and sometimes somewhat more, than indicated. Steam consumption, for instance, varies with different efficiencies of heat insulating covering employed; while cooling water requirements are affected by air content of the injection water and other factors. Any data obtained from this table will be found to agree closely with data generally obtained from actual operation.

<sup>1</sup> In the case of a multiple effect, figures given are for combined evaporation from all effects.

<sup>2</sup> Amount of heating steam supplied to first effect, at pressure of 3.5 lbs., when liquor is fed to evaporator at approximately 120° F. Different steam pressure or reasonably different temperature of feed liquor will affect figures within a few percentage only.

<sup>3</sup> Based on 26-in. vacuum (referred to 30-in. barometer) in last effect. Figures above heavy black line are for parallel current jet condensers; below heavy black line for counter-current cataract condensers. The type of condenser usually employed is as indicated by this statement.



“The object of multiple effect evaporation is simply to reduce the cost of removing the water. The following table shows the economy obtained by means of multiple effect evaporation :—

“**COMMERCIAL FIGURES FOR WATER EVAPORATED PER 100 UNITS OF STEAM**

Steam 100.	Single.	Double.	Triple.	Quadruple.
Water - - - -	95	150	220	300

**COMMERCIAL FIGURES FOR WATER EVAPORATED PER 100 UNITS OF COAL.**

COAL AT 6 : 1

Coal 100.	Single.	Double.	Triple.	Quadruple.
Water - - - -	570	900	1320	1800

Example—1,000 kg. of water evaporated in triple effect.

$$(a) \text{ Steam required} = \frac{1000}{220} \times \frac{100}{1} = 450 \text{ kg.}$$

$$(b) \text{ Coal required} = \frac{450}{6} = 76 \text{ kg.}$$

“Actual working figures taken from a Kestner triple effect evaporator concentrating tan extract liquors show that 2.3 tons of water were evaporated per ton of live steam in the first effect, so that, based on coal at 7.1 in the boiler, 16.1 tons of water are evaporated per ton of coal.”

**Relation of Evaporator to Boilers and Engines.**—In processes involving evaporation, the quantity of steam required for evaporating must be considered when determining boiler capacity, and should also enter into the selection of engines. The following brief discussion is intended to assist in preliminary calculations. The facts presented are approximations and generalisations. For final decision, evaporator experts as well as boiler and engine experts should always be consulted.

One boiler horse power is equivalent to the evaporation of 34.5 lbs. of water from 212° F. to steam at atmospheric pressure. A boiler horse power is also very nearly equal to the evaporation of 30 lbs. from water at 100° F. to steam at 70 lbs. gauge pressure.

From the above is derived the following useful approximation :—

$$\text{Boiler horse power required by evaporator} = \frac{\text{Steam consumption}}{30}$$

The amount of coal needed to generate the steam for the evaporator depends, of course, on the grade of coal and efficiency of grate and boiler.

A coal of 12,500 B.T.U., when boiler and furnace efficiency is 50 per cent., evaporates 6.4 lbs. water from and at 212° F. or 5.6 lbs. from 100° F. feed to 70 lbs. pressure. The same coal, when boiler and furnace efficiency is 60 per cent., evaporates 7.7 lbs. from and at 212° F. or 6.7 lbs. from 100° F. feed to 70 lbs. pressure.

Below are figures relating to the economy (steam consumption per horse-power hour) of different types of steam prime movers. Although statements are given for both condensing and non-condensing practice, it must be remembered that the engine or turbine must be run non-condensing if the exhaust is to be used for running the evaporators. If requirements for the evaporator are equal to or in

excess of the steam needed to run the engine, the engine should be non-condensing. If the requirements for the evaporator are materially less than the steam needed to run the engine, it may sometimes pay to run the engine condensing and take steam for the evaporator direct from the boilers. Each case must be judged on its individual merits.

**Steam Consumption of Engines, Turbines, and Pumps.**—High speed single-valve non-condensing: steam consumption per I.H.P. hour, full load, saturated steam 75-125 lbs. pressure, exhausting at atmosphere or slightly above, ranges from about 27 lbs. to about 50 lbs. Averages for good practice are 30-35 lbs.

High speed multiple-valve simple non-condensing (four-valve non-releasing): steam consumption per I.H.P. hour, full load, steam 75-125 lbs., exhaust atmosphere or slightly above ranges from 22-35 lbs. Averages for good practice are 25-30 lbs.

Low speed multiple-valve simple non-condensing (four-valve releasing Corliss): steam consumption per I.H.P. hour, full load, saturated steam 130 lbs. Average for good practice, 25 lbs.

Non-condensing turbine: a 100-kw. two-stage turbine, using steam at 110 lbs., exhausting to atmosphere, is guaranteed by manufacturer to use not over 51.5 lbs. per kilowatt hour at full load (about 38.4 lbs. per I.H.P. hour).

Compound non-condensing (four-valve Corliss cross compound): steam consumption per I.H.P. hour, full load, steam 150 lbs., exhaust atmosphere. Average for good practice, about 20 lbs.

Direct acting steam pump: simple pumps, running at full load, on saturated steam 90-125 lbs., pressure 5 lbs. exhaust back pressure, use about 100 lbs. steam per delivered horse-power hour.

Compound condensing (Corliss four-valve cross compound): steam consumption per I.H.P. hour, full load, steam 150 lbs., back pressure 2 lbs. absolute. Average practice, 14-15 lbs.

Triple-expansion condensing (Corliss four-valve): steam consumption per I.H.P. hour, full load, steam 150 lbs., back pressure 1.5 lb. absolute. Average practice, about 12-13 lbs.

Condensing turbines: (1) a 500-kw. four-stage turbine, using saturated steam 125 lbs., and exhausting against a 27-in. vacuum, is guaranteed by manufacturer to consume not over 21.2 lbs. per kilowatt hour at full load (about 16 lbs. per I.H.P. hour).

(2) A 2,000-kw. six-stage turbine, steam 185 lbs. and 122° F. superheat, exhausting against a 29-in. vacuum, is guaranteed by manufacturer to consume not over 14.7 lbs. per kilowatt hour at full load. Reducing to an equivalent economy in saturated steam gives about 16.2 lbs. steam per kilowatt hour, or about 12.1 lbs. steam per horse-power hour.

#### CONCENTRATION OF SOLUTIONS

Given a volume  $V$  of a solution of specific gravity  $D$  at 15° C. to be evaporated so that the final specific gravity  $D_1$  at 15° C., then the volume of water evaporated

$$= \frac{V(D_1 - D)}{D_1 - 1}.$$

The percentage evaporation by weight

$$= \frac{D_1 - D}{D(D_1 - 1)} \times 100.$$

Given a solution containing a known percentage  $P_1$  of solids by weight, to be evaporated so that the final percentage by weight of solids is  $P_2$ , then the percentage by weight of the original solution to be evaporated

$$= \frac{P_2 - P_1}{P_2} \times 100.$$

#### MIXTURE OF SOLUTIONS

Having given volumes  $V_1, V_2, V_3$  of solutions having densities  $D_1, D_2$ , and  $D_3$ , to find the density of the resulting mixture,

$$D = \frac{(V_1 \times D_1) + (V_2 \times D_2) + (V_3 \times D_3) + \dots}{V_1 + V_2 + V_3 + \dots}.$$

USEFUL CONSTANTS

1 gal. = 10 lbs. of water at 62° F.  
 1 cub. ft. of water weighs 62.3 lbs.  
 1 cub. ft. of air at 0° C. and 1 atmosphere = 0.0807 lb.  
 1 cub. ft. hydrogen at 0° C. and 1 atmosphere = 0.00559 lb.  
 1 electric unit = 1,000 watt hrs. = 1.34 H.P. hours.  
 1 H.P. = 33,000 ft.-lbs. per minute = 746 watts.  
 1 B.T.U. = 778 ft.-lbs. of wk.  
 1 kg. calorie = 427 kg. metres.  
 Latent heat of steam at 1 atmosphere = 537 kg. calories = 906 B.T.U.  
 1 atmosphere = 14.7 lbs. per sq. in.  
     = 2,116 lbs. per sq. ft.  
     = 760 mm. of mercury column.  
     = 29.62 in. of mercury column.  
     = 33.9 ft.-head of water.  
 1 lb. pressure per sq. in. = a column of water 2.3 ft. high.  
 Column water 1 ft. high = .434 lb. per sq. in.  
 Absolute temperature "T" = ° C. plus 273 or ° F. plus 460° F.  
 1 standard atmosphere (by definition) = 760 mm. of mercury at 0° C. = 29.921 in. mercury  
 at 32° F. = 30 in. mercury at 58.4° F. = 33.90 ft. water at 32° F. = 14.696 lbs. per sq. in.

PRESSURE CONVERSION FACTORS AT 32° F.

	Inches Mercury.	Feet Water.	Lbs. per sq. in.	Atmospheres.
Inches mercury - - -	1.0	1.133	0.491	.0334
Feet water - - - -	0.8827	1.0	0.434	.0295
Lbs. per square inch - -	2.037	2.308	1.0	.0680

Approximate temperature correction factor for height of a mercury column = .0001 per ° F.  
*Example.*—Barometer reads 30 in. at 80° F. To correct reading to 58.4° F. correction  
 = .0001 × 30 × (80 - 58.4) = 0.648 in. Reading at 58.4° F. = 30 in. + .065 in. = 30.065 in.

CONVERSION FACTORS U.S. AND METRIC UNITS

U.S. to Metric.	Metric to U.S.
Inches = 2.540 centimetres Feet = .3048 metre Sq. ft. = .0929 sq. metre Sq. yds. = .836 sq. metre Cub. ft. = .02832 cub. metre Cub. yds. = .765 cub. metre U.S. gallons = 3.7853 litres Pounds = .4536 kilo B.T.U. = 252 gram calories Horse power = 746 kilowatts ° F. = .5555 ft. ° C. To change temperature F. to temperature C., subtract 32 and multiply by 5/9.	Centim tres = 3937 in. Metres = 3.2808 ft. Sq. metres = 10.764 sq. ft. Sq. metres = 1.196 sq. yds. Cub. metres = 35.314 cub. ft. Cub. metres = 1.308 cub. yds. Litres = 1.0567 quarts Kilos = 2.2046 lbs. Kg. calories = 3.9683 B.T.U. Kilowatts = 1.341 H.P. ° C. = 1.8° F. To change temperature C. to temperature F., multiply by 9/5 and add 32.

1 B.T.U. = 777.5 + ft.-lbs.  
 1 H.P. hour = 2,547 B.T.U.  
 1 U.S. gallon = 231 cub. in. = .1337 cub. ft.  
 1 British Imperial gallon = 277.274 cub. in. = 1.2 U.S. gal. = .1604 cub. ft.  
 1 cub. ft. = 7.48 U.S. gallons = 6.24 Imperial gallons.  
 At 4° C. (39.2° F.), 1 cub. ft. water = 62.4 lbs., 1 U.S. gallon water = 8.34 lbs.  
 (Imperial gallon water = 10 lbs. at 62° F.)  
Lbs. per hour = gallons (of water) per minute (approx.).  
 500

## PROPERTIES OF SATURATED STEAM

(29 in. (736.6 mm.) vacuum to 100 lbs. gauge (7.804 atmospheres) pressure.)

Vacuum—Referred to 30-in. Bar. Mercury at 58.4 F.		Temperature.		Specific Volume.		Heat of the Liquid.		Heat of Vaporisation.	
Inches.	Milli- metres. <sup>1</sup>	° F. <sup>2</sup>	° C.	Cub. Ft. per Lb. <sup>2</sup>	Cub. M. per Kilo. <sup>1</sup>	B.T.U. per Lb. <sup>2</sup>	Calories per Kilo. <sup>1</sup>	B.T.U. per Lb. <sup>2</sup>	Calories. per Kilo. <sup>1</sup>
29.0	736.6	79.07	26.11	657.0	41.02	47.11	26.17	1047.2	581.8
28.5	723.9	91.70	33.17	446.2	27.86	59.70	33.17	1040.3	577.9
28.0	711.2	101.15	38.42	339.6	21.20	69.12	38.40	1035.0	575.0
27.5	698.5	108.70	42.61	275.2	17.18	76.64	42.58	1030.8	572.7
27.0	685.8	115.06	46.14	231.9	14.48	82.98	46.10	1027.2	570.7
26.5	673.1	120.55	49.20	200.2	12.50	88.46	49.14	1024.1	568.9
26.0	660.4	125.38	51.88	176.7	11.03	93.28	51.82	1021.4	567.4
25.5	647.7	129.75	54.31	158.1	9.870	97.64	54.24	1018.9	566.1
25.0	635.0	133.77	56.54	143.0	8.927	101.65	56.47	1016.7	564.8
24.0	609.6	140.64	60.38	120.9	7.548	108.51	60.28	1012.8	562.7
23.0	584.2	146.78	63.77	104.5	6.524	114.64	63.69	1009.3	560.7
22.0	558.8	152.16	66.76	92.3	5.702	120.02	66.69	1006.2	559.0
21.0	533.4	157.00	69.44	82.6	5.157	124.86	69.37	1003.4	557.4
20.0	508.0	161.42	71.90	74.8	4.670	129.28	71.82	1000.8	556.0
19.0	482.6	165.42	74.12	68.5	4.276	133.28	74.04	998.5	554.7
18.0	457.2	169.14	76.19	63.1	3.939	137.00	76.11	996.4	553.6
17.0	431.8	172.63	78.13	58.6	3.658	140.50	78.06	994.3	552.5
16.0	406.4	175.93	79.94	54.6	3.409	143.80	79.89	992.3	551.3
15.0	381.0	179.03	81.69	51.2	3.196	146.91	81.02	990.5	550.3
14.0	355.6	181.92	83.29	49.0	3.059	149.80	83.22	988.8	549.3
13.0	330.2	184.68	84.82	45.55	2.844	152.57	84.76	987.1	548.4
12.0	304.8	187.31	86.28	43.2	2.699	155.21	86.23	985.5	547.5
11.0	279.4	189.83	87.68	41.05	2.503	157.73	87.63	984.0	546.7
10.0	254.0	192.23	89.02	39.1	2.441	160.14	88.97	982.2	545.6
9.0	228.6	194.52	90.29	37.4	2.335	162.44	90.24	981.2	545.1
8.0	203.2	196.73	91.52	35.8	2.235	164.68	91.49	979.8	544.3
7.0	177.8	198.87	92.70	34.3	2.141	166.81	92.67	978.6	543.7
6.0	152.4	200.94	93.86	33.0	2.060	168.88	93.82	977.2	542.9
5.0	127.0	202.92	94.96	31.8	1.985	170.89	94.93	976.1	542.3
4.0	101.6	204.85	96.03	30.6	1.910	172.81	96.06	974.8	541.6
3.0	76.2	206.71	97.06	29.55	1.845	174.68	97.04	973.7	540.9
2.0	50.8	208.52	98.07	28.6	1.785	176.50	98.06	972.6	540.3
1.0	25.4	210.28	99.04	27.7	1.729	178.27	99.04	971.4	539.7
0.0	0.0	212.00	100.00	26.8	1.673	180.00	100.00	970.4	539.1

<sup>1</sup> Obtained by conversion from preceding column.<sup>2</sup> Based on values given by Marks and Davis. Interpolated.

1 B.T.U. per lb. = .5555 ft. calorie per kilo.

1 calorie per kilo = 1.8 B.T.U. per lb.

1 cub. ft. per lb. = .06243 cub. metre per kilo.

1 cub. metre per kilo = 16.0184 cub. ft. per lb.

## PROPERTIES OF SATURATED STEAM (continued)

Pressure.		Temperature.		Specific Volume.		Heat of the Liquid.		Heat of Vaporisation.	
Lbs. per Sq. In. Gauge.	Atmospheres (Absolute).	° F.	° C. <sup>1</sup>	Cub. Ft. per Lb. <sup>2</sup>	Cub. M. per Kilo. <sup>1</sup>	B.T.U. per Lb. <sup>2</sup>	Calories per Kilo. <sup>1</sup>	B.T.U. per Lb. <sup>2</sup>	Calories per Kilo. <sup>1</sup>
1	1.068	215.3	101.8	25.23	1.575	183.4	101.9	968.2	537.9
2	1.136	218.5	103.6	23.80	1.486	186.6	103.7	966.2	536.8
3	1.204	221.5	105.3	22.53	1.407	189.6	105.3	964.3	535.7
4	1.272	224.4	106.9	21.40	1.336	192.5	106.9	962.4	534.7
5	1.340	227.2	108.4	20.38	1.272	195.3	108.5	960.6	533.7
6	1.408	229.8	109.9	19.45	1.214	198.0	110.0	958.8	532.7
7	1.476	232.4	111.3	18.61	1.162	200.6	111.4	957.2	531.8
8	1.544	234.8	112.7	17.85	1.114	203.1	112.8	955.2	530.7
9	1.612	237.1	113.9	17.14	1.070	205.4	114.1	954.0	530.0
10	1.680	239.4	115.2	16.49	1.029	207.7	115.4	952.5	529.2
15	2.061	249.7	120.9	13.88	0.8660	218.2	121.2	945.5	525.3
20	2.321	258.8	126.0	11.99	0.7485	227.4	126.3	939.3	521.8
30	3.041	274.1	134.5	9.45	0.5900	243.0	135.0	928.5	515.8
40	3.722	286.7	141.5	7.82	0.4882	255.9	142.2	919.4	510.8
50	4.402	297.7	147.6	6.68	0.4169	267.2	148.4	911.2	506.2
60	5.082	307.3	152.9	5.83	0.3640	277.1	153.9	903.9	502.2
70	5.763	316.0	157.8	5.18	0.3234	286.1	158.9	897.2	498.4
80	6.443	323.9	162.2	4.67	0.2915	294.3	163.5	891.0	495.0
90	7.124	331.2	166.2	4.24	0.2647	301.8	167.7	885.3	491.8
100	7.804	337.9	169.9	3.89	0.2429	308.8	171.6	880.0	488.9

<sup>1</sup> Obtained by conversion from preceding column.

<sup>2</sup> Based on values given by Marks and Davis. Interpolated.

1 B.T.U. per lb. = .5555 ft. calorie per kilo.

1 calorie per kilo = 1.8 B.T.U. per lb.

1 cub. ft. per lb. = .06243 cub. metre per kilo.

1 cub. metre per kilo = 16.0184 cub. ft. per lb.

## CHAPTER IX

# FILM EVAPORATORS

### LITERATURE

J. A. REAVELL. "Evaporation in the Chemical Industry." *Jour. Soc. Chem. Ind.*, 1918, 37, 172 T.

THE types of evaporators discussed in the preceding chapters were of the "pan" type.

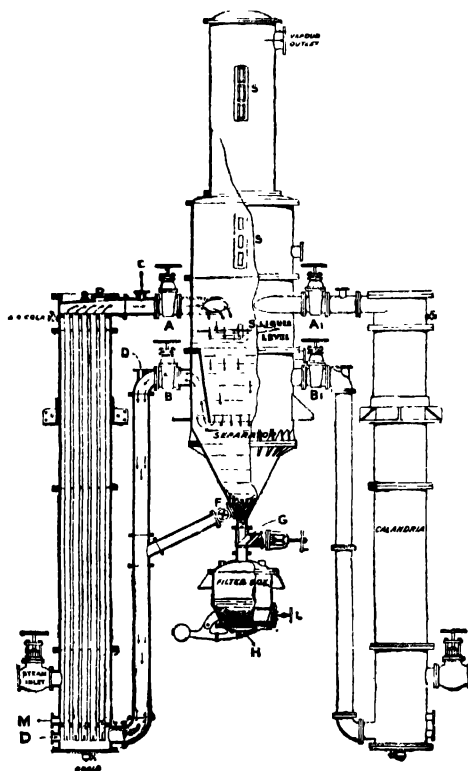
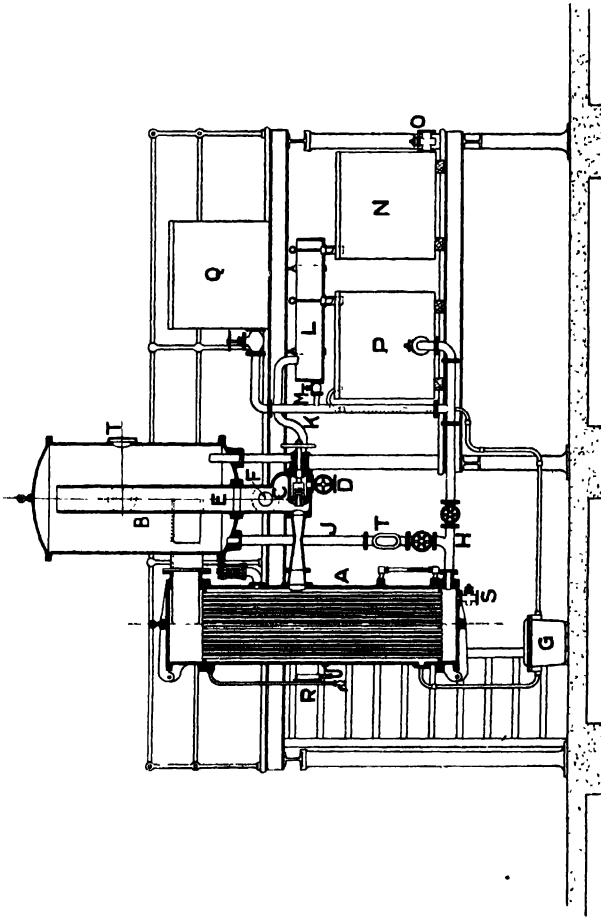


FIG. 35.—Kestner's Patent Desalting Film Evaporator.

Within the last few years the "Film" type of evaporator has made considerable progress, so that a brief account of this type of plant is necessary here.

In the Kestner film evaporator the evaporator tubes are 23 ft. long. The liquid is fed into the tubes from a tank about 3 ft. above the level of the bottom



A	EVAPORATOR
B	SEPARATOR
C	STEAM ECONOMISER
D	LOW STEAM INLET
E	EXHAUST VALVE TO STEAM ECONOMISER
F	EXHAUST VALVE TO ATMOSPHERE
G	STEAM TRAP
H	WEAK LIQUID INLET TO EVAPORATOR
I	CIRCULATING PIPE
J	CONCENTRATED LIQUID DISCHARGE PIPE
K	OUTLET FOR CONCENTRATED LIQUID TO WASH WATER
L	DRAIN FOR RETAINING LIQUID TO EVAPORATOR
M	CONCENTRATED LIQUID TANK
N	CONCENTRATED LIQUID FINAL DISCHARGE
O	CONCENTRATED WATER TANK
P	WEAK LIQUID TANK
Q	AIR DRAIN
R	LIQUID DRAIN ON EVAPORATOR
S	SIGHT GLASS ON LIQUID POOL SEPARATOR

LINE DRAWING OF SIMPLEX PATENT FILM PRESSURE EVAPORATOR  
(SEE SEPARATOR TYPE)  
WITH STEAM ECONOMISER

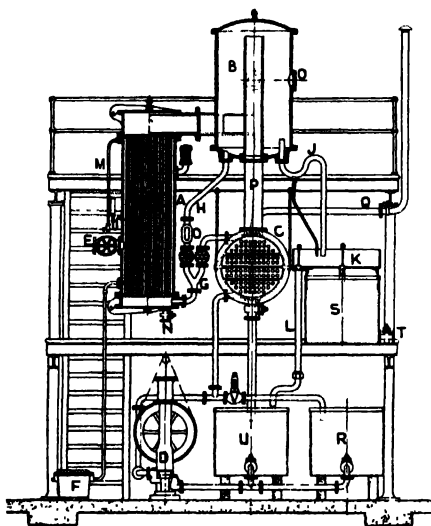
READ OFFICIAL SPECIFICATION  
GOVAN, GLASGOW.  
SCALE: 1" = 1' 6"  
DRAWN BY: J. D.  
CHECKED BY: J. D.  
JOB NO.: 11-2320

Fig. 36.

tube plate, and assuming that this liquid is hot, on steam being applied to the outer surface of the tubes ebullition at once commences inside, releasing a large volume of vapour which must find its way to a region of lower pressure by passing up the tubes. As the result a "climbing film" is produced.

The liquor and vapour, on leaving the top of the tubes, meet a fixed centrifugal baffle, where the liquor is separated from the vapour, the liquor passing to the concentrated liquor tank and the vapour to atmosphere or to the condenser.

The velocity of the liquor passing up the tube—which may attain 30-60 metres per second—is thus used by means of centrifugal action to separate the vapours from the liquid.



A	SEPARATOR
B	SEPARATOR
C	LIQUOR PREHEATER
D	STEAM HEATING LIQUOR FROM PAN
E	STEAM HEATING LIQUOR FROM PAN
F	STEAM HEATING LIQUOR FROM PAN
G	STEAM HEATING LIQUOR FROM PAN
H	STEAM HEATING LIQUOR FROM PAN
I	STEAM HEATING LIQUOR FROM PAN
J	STEAM HEATING LIQUOR FROM PAN
K	STEAM HEATING LIQUOR FROM PAN
L	STEAM HEATING LIQUOR FROM PAN
M	STEAM HEATING LIQUOR FROM PAN
N	STEAM HEATING LIQUOR FROM PAN
O	STEAM HEATING LIQUOR FROM PAN
P	STEAM HEATING LIQUOR FROM PAN
Q	STEAM HEATING LIQUOR FROM PAN
R	STEAM HEATING LIQUOR FROM PAN
S	STEAM HEATING LIQUOR FROM PAN
T	STEAM HEATING LIQUOR FROM PAN
U	STEAM HEATING LIQUOR FROM PAN
V	STEAM HEATING LIQUOR FROM PAN

LINE DRAWING OF SIMPLEX PATENT FILM PRESSURE EVAPORATOR  
WITH LIQUOR PREHEATER

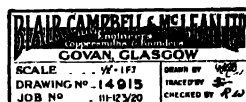


FIG. 37.

The advantage of the system is that the great speed of travel of the liquid and vapour up the pipes and the intimate contact of the moving fluids with the heated surfaces of the calandria, causes an extremely efficient heat transfer.

Also the long "stewing" of the boiling liquid in the pan is avoided, each element of liquid being only heated for a very short time before gasification.

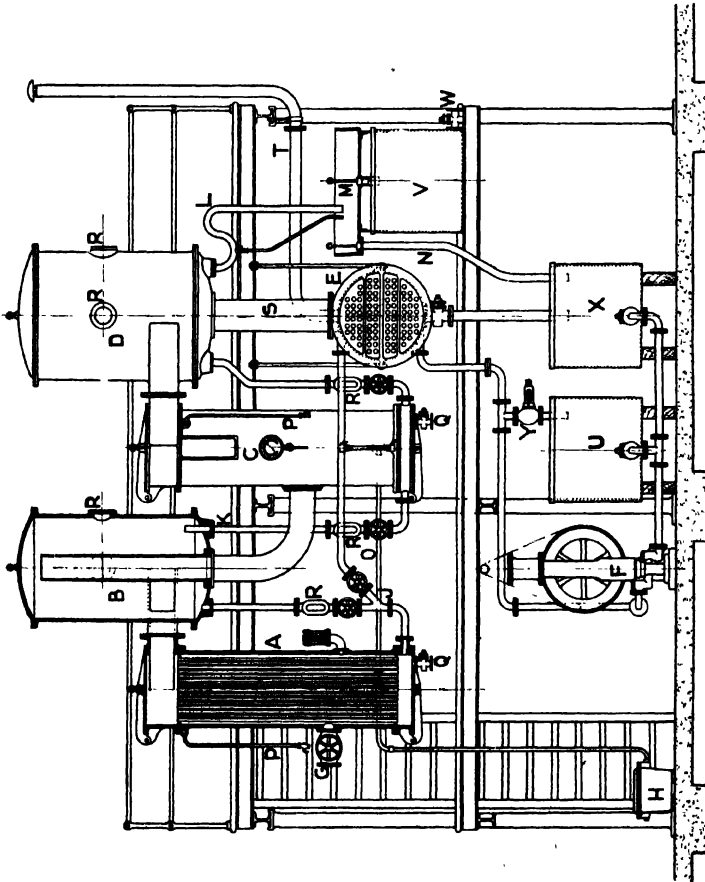
The application of these principles led to the invention of :—

**Kestner's Patent Desalting Plant.**—The Kestner Desalting Evaporator, illustrated in Fig. 35.

The separator ss is filled with the lye to be evaporated to above the opening b, the height of the liquor being seen through the sight glasses. The steam is turned on at n in the calandria A, which consists of a number of pipes running through a steam box, as shown in the drawing.

The liquor from the separator s then passes through b down into the bottom





A	1 <sup>ST</sup> EFFECT SEPARATOR
B	2 <sup>ND</sup> SEPARATOR
C	3 <sup>RD</sup> SEPARATOR
D	LIQUOR PREHEATER
E	STEAM DRIVEN LIQUOR FEED PUMP
F	TRAP
G	INLET TO 1 <sup>ST</sup> EFFECT SEPARATOR
H	MAIN LIQUOR INLET TO 1 <sup>ST</sup> EFFECT SEPARATOR
I	LIQUOR FEED BETWEEN EFFECTS
J	CONDENSER
K	STEAM JACKET FOR CONDENSER
L	STEAM JACKET FOR CONDENSER
M	STEAM JACKET FOR CONDENSER
N	STEAM JACKET FOR CONDENSER
O	STEAM JACKET FOR CONDENSER
P	STEAM JACKET FOR CONDENSER
Q	STEAM JACKET FOR CONDENSER
R	STEAM JACKET FOR CONDENSER
S	STEAM JACKET FOR CONDENSER
T	STEAM JACKET FOR CONDENSER
U	STEAM JACKET FOR CONDENSER
V	STEAM JACKET FOR CONDENSER
W	STEAM JACKET FOR CONDENSER
X	STEAM JACKET FOR CONDENSER
Y	STEAM JACKET FOR CONDENSER
Z	STEAM JACKET FOR CONDENSER

LINE DRAWING OF MULTIPLEX PATENT DOUBLE EFFECT PRESSURE EVAPORATOR

(See. by Soc. Inst.)

WITH LIQUOR PREHEATER.

W. & A. GIBBS & CO. LTD.  
GLASGOW, SCOTLAND.  
SCALE: 1/4" = 1'-0"  
DRAWING NO. 14 916  
JOB NO. 112328

FIG. 38.

box of the calandria A, then boils up the tubes, and rushes back as vapour or liquid through A into the separator.

There thus takes place a continuous circulation of liquor through the separator and calandrias, and as crystals of salt form in the separator they fall down the central space formed by the circular baffle, any salt which crystallises out falling to the bottom of the cone, while the liquor passes through the outlet B, at which point it is practically free from salt. There may be as many as four calandrias connected to one separator, one being used for washing out or cleaning while the others are in action.

At the bottom of the separator is a valve G, by means of which accumulated salt is periodically run into the filter box; the valve G being closed, the mother liquors run off at H, and the salt is removed from the box by means of the discharge doors I.

**The Simplex Patent Film Evaporator.**—A somewhat similar type of plant is manufactured by Messrs Blair, Campbell, & M'Lean, of Glasgow, for the concentration of liquors which do not deposit salts during concentration, for instance such liquors as Solvay and Leblanc caustic soda, caustic potash, and other trade liquors in the chemical industry, and some line drawings are appended which illustrate its action.

The weak liquor to be concentrated is fed into the apparatus from an overhead liquor tank Q (see Fig. 36), the quantity being regulated by a special valve H fitted with an indicating device.

The liquor, if fed in at a temperature closely approaching its boiling point, rises to a uniform height in the evaporator tubes contained in the evaporator A and immediately begins to boil, giving off vapour.

As soon as ebullition takes place at the lowest portion of the heating tubes, the vapour forms bubbles to start with, but as its volume steadily increases with a corresponding high velocity, the liquor attaches itself to the tube walls in the form of a uniform film, the vapour forming a central core, and both liquor and vapour enter the separator B through the tangential inlet at a high velocity.

On account of the centrifugal action produced in the separator B, the heavier particles of liquid are separated from the vapour and flow down the walls of the separator, collecting on the bottom and finally flow back into evaporator via the pipe J. The vapour, however, passes away from the separator, being drawn off through the vertical vapour pipe E inserted in the central line of the separator, and is exhausted through F to the atmosphere or to jet condenser and vacuum pump or to second effect evaporator, or it may be utilised for preheating the liquor entering the still or even reinjected by a steam compressor C back into the evaporator.

The amount of liquor returned to the evaporator is controlled by a valve, and depends upon the degree of concentration desired. The degree of concentration is primarily controlled by means of the regulating valve in the weak liquor inlet pipe below the sight glass T.

The concentrated liquor flows away from the bottom of the separator B via the pipe K, the cooling gutter L, into the concentrated liquor tank N.

A draining cock M allows concentrated liquor to be returned to the evaporator.

The condensed steam from the jacket of the evaporator is taken through the steam trap G and is fed to the condensed water tank P.

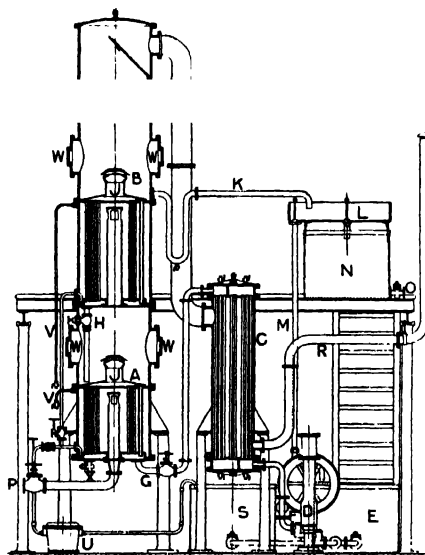
Fig. 37 shows the same plant, but fitted with a tubular preheater C which warms the lye entering the evaporator A.

In this plant the cold liquor in the feed tank R is forced by the pump D through the tubular preheater C, where it is preheated by the vapours coming away from the separator B down the pipe P (thus serving the double purpose of partially condensing these vapours from B and preheating the liquor entering the evaporator A via the inlet G).

Fig. 38 shows the same apparatus arranged for double effect evaporators. The vapours from the separator B pass directly into the steam jacket of the second evaporator C, the condensed liquor being drawn away via the steam trap H.

The vapours from the second evaporator C then pass into the separator D, which is fitted up precisely as the preceding plant.

Fig. 39 shows another double effect evaporator of the same type as that described above, but the evaporators A and B are superimposed one above the other in a single column.



- A. C. EFFECT
- B. C. EFFECT
- C. LIQUOR PREHEATER
- D. STEAM DRIVEN LIQUOR PUMP
- E. HEAT LIQUOR TANK
- F. STEAM VALVE ON PUMP
- G. LIQUOR PUMP & VALVE
- H. LIQUOR PUMP & VALVE
- I. LIQUOR PUMP & VALVE
- J. LIQUOR PUMP & VALVE
- K. LIQUOR PUMP & VALVE
- L. LIQUOR PUMP & VALVE
- M. LIQUOR PUMP & VALVE
- N. LIQUOR PUMP & VALVE
- O. LIQUOR PUMP & VALVE
- P. LIQUOR PUMP & VALVE
- Q. LIQUOR PUMP & VALVE
- R. LIQUOR PUMP & VALVE
- S. LIQUOR PUMP & VALVE
- T. LIQUOR PUMP & VALVE
- U. LIQUOR PUMP & VALVE
- V. LIQUOR PUMP & VALVE
- W. LIQUOR PUMP & VALVE
- X. LIQUOR PUMP & VALVE
- Y. LIQUOR PUMP & VALVE
- Z. LIQUOR PUMP & VALVE

**MULTIPLEX PATENT DOUBLE EFFECT PRESSURE EVAPORATOR  
(SUPERIMPOSED TYPE) WITH LIQUOR PREHEATER**

GOVAN, GLASGOW  
SCALE  
DRAWING NO. 14917

FIG. 39.

The weak liquor to be concentrated is pumped from the store tank E via the pump D, through the preheater C (where it is preheated by the vapours coming from the second effect down the pipe Q).

The heated liquor then passes via the pipe G into the evaporator A and is boiled, as above described, by the heat of the steam jacket by which A is surrounded.

The vapours and liquid are separated in the separator J, the hot vapours passing onwards and serve as the heating medium for the boiling tubes of the second effect B, the condensed water being drawn off by a small pipe. The concentrated liquor remaining on the first effect collects at A, and by means of the pipe H can be passed up into the second evaporator B, where the same process can be repeated.

## CHAPTER X

MANUFACTURE OF CRUDE GLYCEROL  
FROM SAPONIFICATION, AUTOCLAVE,  
TWITCHELL, AND FERMENTATION  
GLYCEROL

GLYCEROL is also obtained in the splitting of fats into fatty acids by the old process of **lime saponification** used by candle-makers, also by the **acid saponification process** and the more modern processes involving the use of the **Twitchell reagent** and by the use of the **Connstein ferment process** and by the fermentation of sugars.

**Kreibitz's process** for manufacturing soap (by double decomposition of a calcium soap with sodium carbonate) is still worked in the United States and yields a good glycerol water (see Section I., p. 4).

All these processes yield aqueous solutions containing glycerol, *but comparatively free from salt*. The solutions contain as impurities fatty acids, albuminous matters, and sometimes metallic soaps, which must be removed before concentration, otherwise foaming and entrainment of liquid will result.

The glycerol waters are subjected to a preliminary purification, usually boiling to coagulate the protein matter, treatment with sulphuric acid to liberate any fatty acids from unchanged fats, and precipitation of such matter by means of lime, alum, or iron salts, according to the process by which the glycerol was obtained.

The liquid is then neutralised and filtered as previously described. The liquid at this stage is sometimes clarified by means of charcoal.

The solution is now concentrated in vacuum apparatus. Since practically no salt is present, the evaporator is used without a salt extractor. Single, double, or triple effect evaporators may be used.

The liquid is concentrated under a pressure of 5-10 cm. of mercury. The boiling point slowly rises to 100°-110° C., until the glycerol is concentrated to about 28° Bé. (sp. gr. 1.240). It then contains about 90 per cent. of pure glycerol.

The glycerol is then further purified by distillation with superheated steam, decolorisation with charcoal, and concentration *in vacuo*, as has been described in Chapter II., Section I., when dealing with distillation of crude soap lye glycerol.

The following notes on the treatment advisable in working up the various crude glycerols derived from different processes of manufacture will be interesting :—

**Crude Lime Saponification Glycerol** (see p. 3, Section I.).—This represents the very best quality of the crude glycerols and contains from 5-17 per cent. of glycerol. The liquor is neutralised with dilute sulphuric acid, filtered from the precipitated calcium sulphate, and concentrated in a vacuum evaporator until it contains 85-90 per cent. of glycerol, and possesses a specific gravity of 1.240-1.242 (28° Bé.). It is then known as "**28° Bé. Saponification Crude**" or "**Candle Crude**" glycerol. Such a crude glycerol contains up to 0.3 per cent. of ash

( $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ , according to the process of manufacture) and yields only a slight precipitate with basic lead acid, and should not contain much organic impurity. It should possess a sweet taste and range in colour from yellow to dark brown. It may readily be distinguished from soap lye crude glycerol by the absence of salt (*i.e.*, no white precipitate with silver nitrate).

A crude glycerol of equal quality is obtained by the **Kreibitz process** of making soap (see Vol. II., Section VI., p. 14) by decomposing a lime soap with sodium carbonate, provided that the original fatty matter is of good quality.

When inferior greases are used, however, the crude glycerol may contain from 1.5 (or more) per cent. of ash, 75.85 per cent. of pure glycerol, and much organic impurity. Such crude glycerol may ferment on storing, yielding trimethylene glycol.

**Crude Distillation Glycerol** (see p. 4, Section I.).—The glycerol water resulting from **acid saponification methods** may be worked up in the same general way as described above under **Saponification Glycerol**. Owing, however, to the large amount of sulphuric acid used in the process, the water is made alkaline by the addition of **lime**, the liquid filtered from the sludge of calcium sulphate which separates, and is then evaporated.

The concentration is usually performed in two stages, first to a density of 32° Tw. (20° Bé. = sp. gr. 1.160), when the large amount of calcium sulphate dissolved in the liquid is allowed to separate, and finally to 48° Tw. (28° Bé. = sp. gr. 1.240), when it contains from 84.86 per cent. of glycerol.

The process of evaporation is complicated by the fact that the calcium sulphate separates out, especially when the crude liquor approaches the specific gravity of 1.240, and coats the heating surface of the evaporator in the form of a hard crust, thereby diminishing the evaporative efficiency. Hence most tube evaporators are almost useless for concentrating the liquors, and a type of evaporator is advisable which allows of the heating surface to be continuously scraped, so as to be kept free from the crust.

Lewkowitsch has designed an evaporator fitted with a revolving heater for use with such liquids.<sup>1</sup>

The **finished crude glycerol** is known in commerce as "**Distillation Glycerol, 28° Bé.**" It contains as a rule the *high ash* content of 2.35 per cent.—principally due to the presence of calcium sulphate, the solvent power of glycerol for this substance being increased by the organic impurities present. The amount of **organic** impurities may often amount to 2 per cent. (according to the quality of fats used in the process of saponification and the care with which the process was carried out).

This type of crude glycerol is therefore much more impure than crude "**saponification glycerol.**"

The colour is usually pale yellow, the taste sharp and astringent, and the smell when rubbed between the hands is unpleasant. Tested with hydrochloric acid, a turbidity appears owing to the presence of fatty acids, while basic lead acetate gives a heavy precipitate.

**Twitchell Crude Glycerol** (see p. 4, Section I.).—This crude glycerol is obtained from the acid waters obtained from **Twitchell's saponification process**. The liquid is neutralised with lime or barium hydrate, in order to precipitate the dissolved sulphuric acid as completely as possible, filtered, and concentrated to a specific gravity of 1.24 (28° Bé., 48° Tw.), as described above under **Crude Distillation Glycerol**, where the same difficulties as regards the presence of calcium sulphate occur if lime is used for neutralisation.

The crude glycerol thus obtained is of good quality, provided the fats used for saponification are first class. It contains, however, more "ash" and, moreover,

<sup>1</sup> See Lewkowitsch, "Evaporation *in vacuo* of Solutions containing Solids," *Jour. Soc. Chem. Ind.*, 1905, 1149; English Patents, 28,747, 1897; 30,616, 1897.

has a somewhat more unpleasant taste than **crude candle glycerol**, so that it fetches a lower price than the latter. A typical analysis showed 85 per cent. glycerol and 0.5 per cent. ash; sp. gr. 1.240.

Sometimes, however, the Twitchell process is applied to **low-class fats**, such as **garbage fats** and greases, a class of goods for which it is specially suitable. Naturally the resulting **crude glycerol** is very poor, containing so much organic impurity that by itself it cannot be worked up for dynamite glycerol.

Such a glycerol of sp. gr. 1.241 may contain 0.5 ash, organic impurities 1.9 per cent., and glycerol 87 per cent. It should be valued on the basis of the impurities it contains.

**Connstein Fermentation Crude Glycerol** (see p. 4. Section 1.).—The glycerol water obtained by splitting fats by means of the lipase contained in castor seed is always rich in albuminoid and other organic impurities.

The liquid may be precipitated with lime, which is stated to remove completely the poisonous alkaloid present in the castor seed (see "Atti del VI. Congresso Internazionale Roma," 1907).

Usually the liquor is filtered through charcoal, which absorbs the bulk of the albuminoids and other organic impurities; but it still remains dark in colour with an unpleasant taste and smell.

The crude glycerol may contain 85 per cent. pure glycerol, 0.5 per cent. of ash, 1.5 per cent. of albuminoids and organic impurities, and be of sp. gr. 1.23-1.24. It can best be refined by distillation.

**Sugar Fermentation Process.**—Recently glycerol has been produced by the fermentation of sugar. The process of procedure is fully described below in a separate chapter.

According to *Krauss* and *Hofmann* (German Patent, 310,606, 1918), fermentation glycerines and crude glycerines from partially decomposed fats such as are present in fish residues, etc., contain a large amount of impurities, especially esters of mono- and polyhydric alcohols and nitrogenous compounds of variable composition, which for the most part are not decomposed during the ordinary treatment of the glycerine. Decomposition may, however, be effected by heating the crude glycerine (to, e.g., 100°-120° C.) with excess of an alkali or alkaline earth hydroxide prior to distillation, or in the case of the glycerine water prior to concentration.

## SECTION II

# The Manufacture of Distilled Glycerol





## CHAPTER I

# SOAP LYE GLYCEROL (*continued*).—DISTILLATION OF THE CRUDE GLYCEROL—GENERAL OUTLINE OF MODERN PROCESS

### Process of Distillation

THE **Crude Soap Lye Glycerol**, obtained as described in the last chapter, is now distilled, either by the producers themselves, or more usually it is sold to firms engaged in the refined glycerol trade and distilled by them under vacuum with the aid of steam, which in old plant usually entered at about 320° F., passing out through a small coil. In modern plant superheated steam is used. Formerly the still was heated directly with a coal or coke fire, and in the fire space is a superheater, consisting of a coil of pipes through which high pressure steam (120-150 lbs. per sq. in.) from the boiler is passed. In modern plant the heating is effected by closed steam coils (200 lbs. pressure), while open superheated steam (210° C.) is used for distilling, thus avoiding charring.

The distillation is usually carried out at 178°-180° C. (352°-356° F.), but as the evaporation proceeds the temperature gradually increases to 199° C. (399° F.). In order to prevent the deposition and burning of salt on the still bottom during the process of distillation, many stills were provided with a false bottom supported about 1 ft. from the base of the still.

Patents have been taken out for agitating the contents of the still with an agitator fixed therein, so as to avoid burning. Usually 5 per cent. of glycerol is lost by decomposition, etc.

The plant is so arranged that the still does not become overheated, otherwise glycerol would be lost by carbonisation and tarry bodies would be produced which would injuriously affect the colour, taste, and odour of the distilled glycerol. The stills are usually provided with "catch-alls" and similar devices for obviating loss of glycerol.

The vacuum employed is usually 25 in., although individual practice varies widely.

The method of effecting the distillation varies widely. Some manufacturers work off in one batch a certain amount of **crude glycerol** (depending on the capacity of the stills), but many prefer to feed the crude glycerol into the still continuously as the glycerol distils off, keeping the level of the liquid in the still nearly constant.

The distillate passes over into a row of condensers, each of which is connected to a receiver. The condensing capacity must be ample, leaving a wide margin of safety.

The fractions obtained are of varying strengths and quality. The weakest fractions—those with a density less than 1.070 (14° Tw., or 9.4° Bé.)—must be returned to the glycerol "treating tanks."

The other portions are run into a vacuum vessel and concentrated by means of a dry steam coil or otherwise under a 28-in. vacuum.

When sufficiently concentrated, about 0.5 per cent. of good animal charcoal is

## 4 THE MODERN SOAP AND DETERGENT INDUSTRY

added to the hot glycerol (say at 80°-100° C.), well agitated and the liquid then pumped through a filter press, as described below.

This decolorised glycerol is known as "**dynamite glycerol**." It varies in colour from pale yellow to deep yellow, possesses a specific gravity of 1.261-1.263, and must conform to certain rigid specifications which are described in another place. It contains, however, small amounts of impurities which renders it unfit for pharmaceutical or dietetic purposes. It must be distilled in order to produce **chemically pure glycerol** (see below).

In general, chemically pure glycerol is prepared by distilling the glycerine without concentration, there being no necessity to concentrate. It is only in producing dynamite glycerol that concentration is necessary after the distillation of the crude glycerol.

Distilled glycerols vary in colour from water-white to yellow, with specific gravities from 1.220-1.260.

All **distilled glycerols** naturally contain very little ash, and on this account their exact percentage of glycerol can be judged from their specific gravities.

**Chemically pure glycerol** or "**double distilled glycerol**" is produced by redistilling "once distilled glycerol" and rejecting all fractions which act on silver nitrate, and do not conform to other special tests detailed below.

The distillate is concentrated, treated with animal charcoal, and filtered. It should then be water-white and of the B.P. standard.

**Chemically pure glycerol** occurs in commerce in different concentrations or strengths, *e.g.*, sp. gr. 1.24, sp. gr. 1.25, and sp. gr. 1.26. It should be odourless, colourless, and possess a pure, sweet taste.

The exact details of the various processes for manufacturing distilled glycerol are usually regarded as valuable trade secrets and so are not accessible to the ordinary technologist.

*Lewkowitsch* ("Technology of Oils, Fats, and Waxes," 1915, iii. 375) goes so far as to state: "The successful distillation of crude glycerine does not depend so much on the kind of apparatus used as on the skill and care of the operator"—a view which the present writer believes to be quite incorrect under modern conditions, especially since the introduction of properly trained chemical engineers into industry, since a well-designed modern plant operated with ordinary skill will produce excellent glycerol with little trouble. However, it is obvious that if the still is not properly handled (or is badly designed) the once distilled glycerol will be so badly impregnated with sodium chloride and various organic impurities such as trimethylene glycol and volatile acids, that a second distillation is necessary.

This means, naturally, a great loss of yield and increase of expense which would be more than counterbalanced were the manufacturer to employ properly trained chemical engineers and properly designed plant.

The losses caused by unsatisfactory distillation may range from 15-40 per cent. The main losses are due to overheating the still, with destruction of the glycerol and the formation of volatile organic acids and acrolein and polyglycols. The organic acids and acrolein contaminate the distillate, while the polyglycols remain behind in the still residues or **glycerol foots**.

## CHAPTER II

# DESCRIPTION OF DIFFERENT TYPES OF MODERN PLANT AND PROCESSES FOR DISTILLING GLYCEROL

### LITERATURE

For an account of early patents and work up to 1900, see G. E. DAVIS, *Jour. Soc. Chem. Ind.*, 1900, **19**, p. 116.

See also J. F. HINCKLEY. *Jour. Soc. Chem. Ind.*, 1907, **26**, 597.

G. A. MOORE, *Jour. Met. Eng. Chem.*, 1910, **2**, 283.

T. H. GRAY. "The Historical Development of the Distillation of Glycerine." *Jour. Soc. Chem. Ind.*, 1922, **41**, 279 R.

E. BRIGGS. "The Distillation of Glycerine," article in Sidney Young's *Distillation Principles and Processes*. Macmillan, 1922.

See also Patents in text.

### Description of Modern Plant for Distilling Glycerol

A VERY large number of special apparatus and stills have been patented for distilling glycerol, some of which are described below:—

### HISTORICAL

G. F. Wilson, of Price's Candle Co., made a notable advance by distilling candle-works' "sweet liquor," using preheated copper stills of 10-30 cwt. capacity and air condensers. This process is wasteful owing to the high temperatures necessary, but it was used until the introduction of the modern steam-heated stills.

The patents of G. F. Wilson (1854), Wilson and Payne (1855), and E. T. Hughes (1859) cover this period of progress.

The extension of the use of glycerol for making dynamite and other blasting explosives led to considerable activity in the design of apparatus and patents.

The first important patent of this period is that of F. J. O'Farrel (1881), who patented the use of a vacuum and pump for distilling crude soap lye in steam at 200° C. (see *Jour. Soc. Chem. Ind.*, 1883, p. 543).

Armondy (*Jour. Soc. Chem. Ind.*, 1882, p. 371) also suggests distilling glycerol under a vacuum.

Payne (1882 *loc. cit.*, p. 459) distils the glycerol and purifies it by passing the glycerine and aqueous vapours through one or more long cylindrical chambers heated to 300°-400° F. The pure glycerol, free from steam, collected in the bottom chambers.

Patents were also issued to Clark (1881), O'Farrel (1883), A. M. Clark (1884).

Brookes (English Patent, 5,882, 1885) describes: "The still and superheating coil are heated by the same furnace, and the former is connected with condensing coils which terminate in vacuum pans large enough to hold the whole charge. The series of condensing coils end in a surface condenser connected with a vacuum pump."

Hagemann in 1885 patented dephlegmating columns for glycerol, fitted with perforated plates and a reflux coil.

Unglaub (English Patent, 8,196, 1889) patented a fractionating column for glycerol similar to an ammonia still.

A notable advance was made by the Belgian Van Ruymbeke (1893) (see English Patents, 24,550, 1893, and 12,367, 1894), who patented the master idea of using a high pressure steam coil for heating the still, thus dispensing completely with direct fire heating. This, in conjunction with the use of expanded reheated steam for the actual distillation, largely reduced the decomposition of the glycerol. The still is described in some detail below.

Scott's Patent (15,159, of 1899) constitutes the next notable step.

## 6 THE MODERN SOAP AND DETERGENT INDUSTRY

*W. E. Garrigue's* still (English Patent, 24,100, 1905) represents a more complicated but very economical plant as regards heat consumption. This is described below in detail.

*F. J. Wood's Plant* (English Patents, 21,658, 1907, and 24,920, 1913) is also complicated in design but economical as regards steam, the main idea being to work from one to six stills with one jet of steam.

In 1919 the *Société Française des Glycerines* (English Patent, 125,574, 1919) patented a plant designed to work without the use of free steam. The crude glycerine at  $180^{\circ}\text{C}$ . is sprayed in an atomised state by means of suitable jets from one vessel to another vessel of still higher vacuum. The temperature is kept at  $180^{\circ}\text{C}$ . The patent is described below.

The author proposes here to give details of some modern plant used for the distillation of glycerol.

In any case the exact results obtained depend not only upon the plant but also upon the skill with which the operator uses same.

Naturally, however, a well-designed plant enables an operator to achieve more easily a good quality glycerol.

In more recent plant the coke fire is replaced by steam heating, as the loss of glycerol in direct fired stills is heavy when crude glycerine is distilled, owing to the salt separating out and settling on the bottom of the still, producing local overheating and decomposition of the organic compounds; much glycerol is thus destroyed, acrolein and other products being produced.

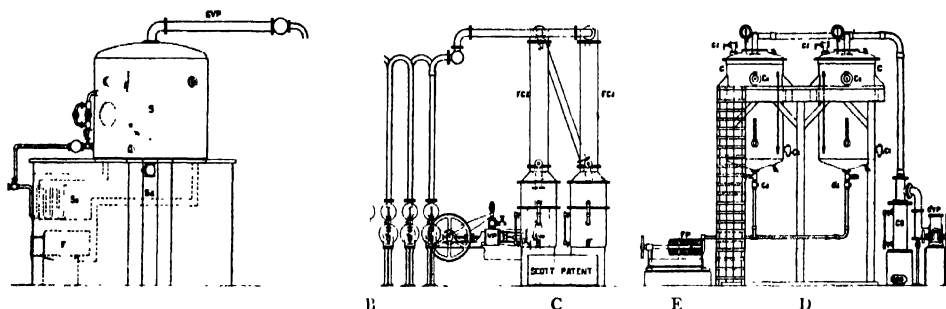


FIG. 2.—Flow Sheet of Scott's Glycerol Refining Plant.

The results are much better with saponification glycerine, although even here very great care is necessary for controlling the fire and free steam if a good distilled glycerol is to be obtained.

**Scott's Fractional Glycerol Still** (see English Patent, 15,159, 1899).—The crude glycerol separated from the salt, as previously described in the foregoing chapters, must now be distilled in order to obtain it pure.

Fig. 1 shows a general view of a small size **Scott glycerol still**, showing the air condensation columns whereby different fractions can be drawn off. Fig. 2 shows a flow sheet of the whole process, while Fig. 3 shows the ground plan of a 50-ton refining plant.

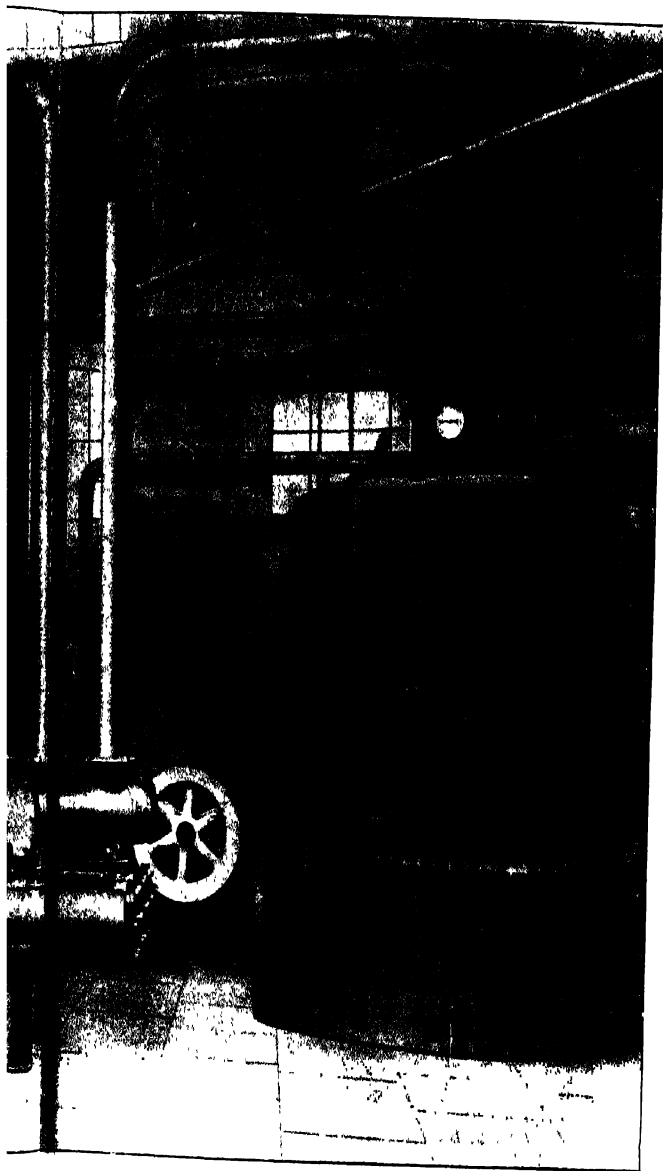
The still A (Fig. 2) may be heated by coke or gas firing, and is supplied with a perforated coil whereby superheated steam at a temperature of  $160^{\circ}\text{C}$ . is blown through the glycerol in the still. The superheating of the steam may be effected by fire or gas, and is automatically controlled by a special damper. In the figure, S is the still, F the fireplace, while the superheating arrangement of the steam is shown at the side.

The glycerol distils over and enters the series of air-cooled condensers B, whence as many as seven complete fractions may be obtained simultaneously. These fractions are usually combined by the operator, but the means is thus obtained of separating any impurities which may be present in the distillate in the smallest possible quantity of glycerol, thus enabling the bulk of the distillate to be concentrated immediately to the marketable article.

Any distillate not condensed by the air-coolers B pass over to C, where complete







U.S. Glycerol Refining Plant

SEC. II.

[To face page 6.





condensation of steam, etc., is effected by the aid of cooling water if necessary. The condensers *c* are connected with the vacuum pump, whereby a high vacuum is maintained throughout the system.

The yield of distilled glycerine is in modern plant as high as 97½ per cent.

The distilled glycerol is now mixed with the correct amount of charcoal for decolouring, and concentrated to the right concentration in the vacuum evaporators *D*, and finally filtered from the charcoal through the filter press *E*.

Fig. 3 shows a ground plan of the scheme of operations: 1, 2, 3, 4 are the crude glycerol storage tanks, whence the glycerol is fed into the stills 6, 7, 8; 9, 10, and 11 represent the fractionating air-cooled columns, 12 the final water-cooled condenser, and 13 the vacuum pump; 14, 15, 16, and 17 represent the distilled glycerol storage tanks, whence the distilled glycerol, mixed with the requisite amount of decolorising carbon, is fed into the vacuum concentrators 18 and 19, the concentrated product being then run out at the bottom of the stills and freed from carbon by the filter presses 20 and 21; 22 represents the condenser for the concentrators 18 and 19; while 23 is the vacuum pump for the concentrators. The cost of evaporation was about £1 per ton of glycerol in 1914.

**Blair, Campbell, & M'Lean's still for glycerol** is indicated in Fig. 4, which shows the arrangement for concentrating the distilled glycerol.

It differs in several respects from Scott's still.

The superheated steam passes into the glycerol through the valve 4, the vapours of steam and glycerol pass up the pipe 8 and 11 through the catch-all 12, where any condensed liquid may run back through 13 to the still; 16A, 16B, 16C are the condensers connected by means of the pipes 15A, 15B, and 15C. The distillates may be collected in the drums 19A, 19B, 19C, which are so connected that one drum may receive the liquid condensed in either of the two condensing columns, as indicated in the figure.

The uncondensed steam, still containing about 2½ per cent. of glycerol vapours, is finally condensed in the water-cooled condenser 24, a weak solution of glycerol being obtained from this condenser; 35 represents the vacuum pump.

The glycerol distilled over is treated with charcoal in the concentrator 40, as previously described, in order to decolorise it, and is then filtered from the charcoal by means of the filter press 42, a small duplex pump being used to pump the liquid from the concentrator 40 through the filter press.

The concentrator is connected up to the vacuum pump 35 with the interposition of a catch-all vessel 38.

**Heckmann's Still for Distilling Glycerine.**—Fig. 5 shows a glycerol distilling plant designed by Heckmann (German Patent, 61,547), and much used in Germany. Glycerol is boiled in *a* by a current of superheated steam at 200°–300° C., a high vacuum being maintained by a pump attached to *KK*, which lowers the boiling point of the liquid in *a* to about 200° C. The glycerol vapours and steam pass away through *G* into the rectifying column *CE*, to which is attached the *dephlegmator* *F*. The liquid condensing in *c* is maintained at about 80° C. by means of the steam-jacketed bottom *D*, so that the water scarcely condenses at all in this part of the apparatus, but passes away as steam, mixed with glycerol vapours, through the bell condensing trays in *e*, into the dephlegmator *F*, and finally reaches the catch-all *A*, where any condensed glycerol runs back through *L* into *c*, and is again distilled there. Consequently only concentrated glycerol collects in *c*, while steam and a very small amount of glycerol vapours pass over from *G* into the condenser *H*, the specific gravity of the water condensing in *H* being checked by a swimming hydrometer contained under a glass bell jar *J*, which should always register less than 1° Bé. The glycerol in *c* is then withdrawn and decolorised with blood or animal charcoal (which has been carefully freed from mineral matter by extracting for weeks with HCl and washing with water).

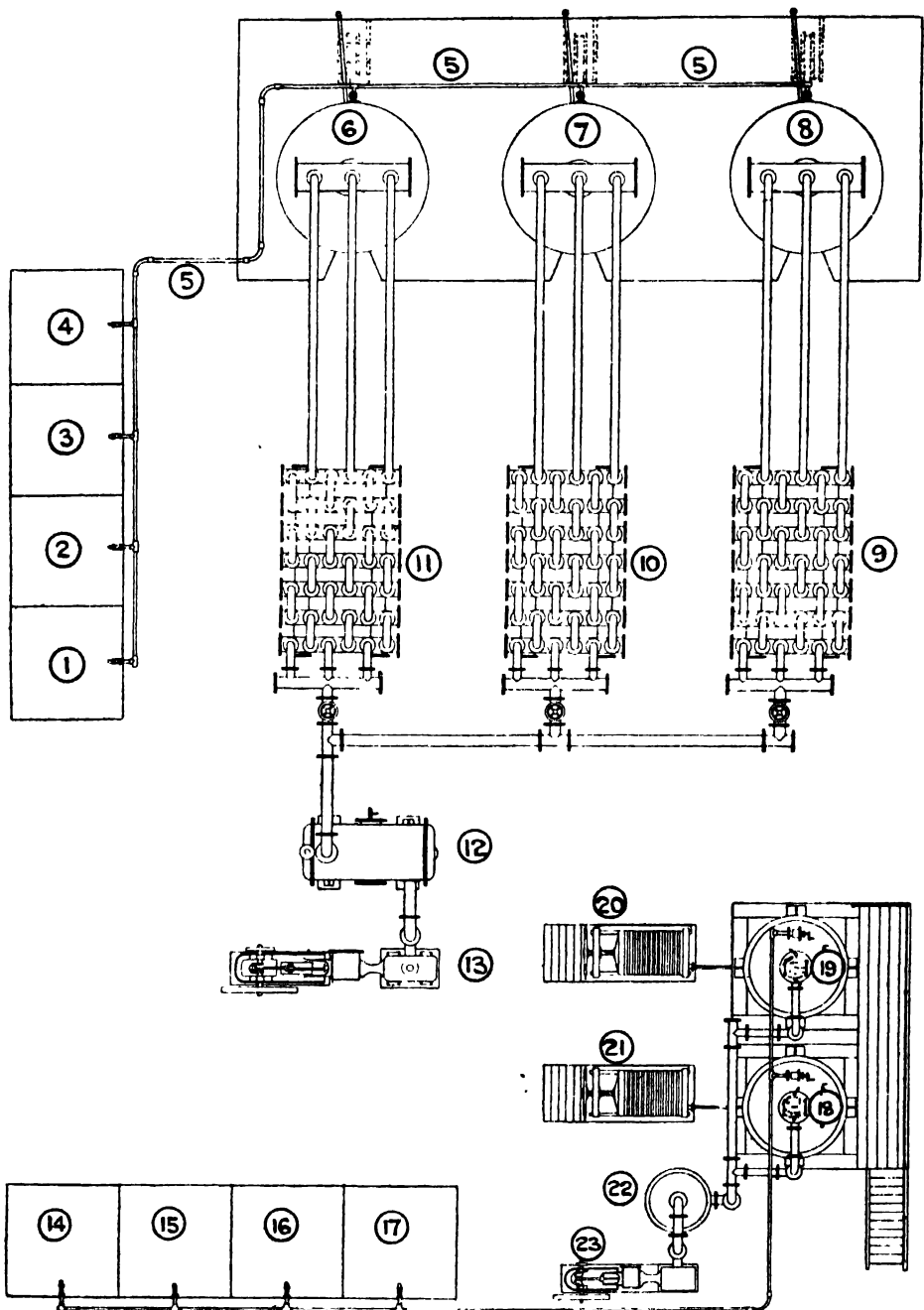


FIG. 3.—Ground Plan of Scott's 50-Ton Glycerol Distillery.

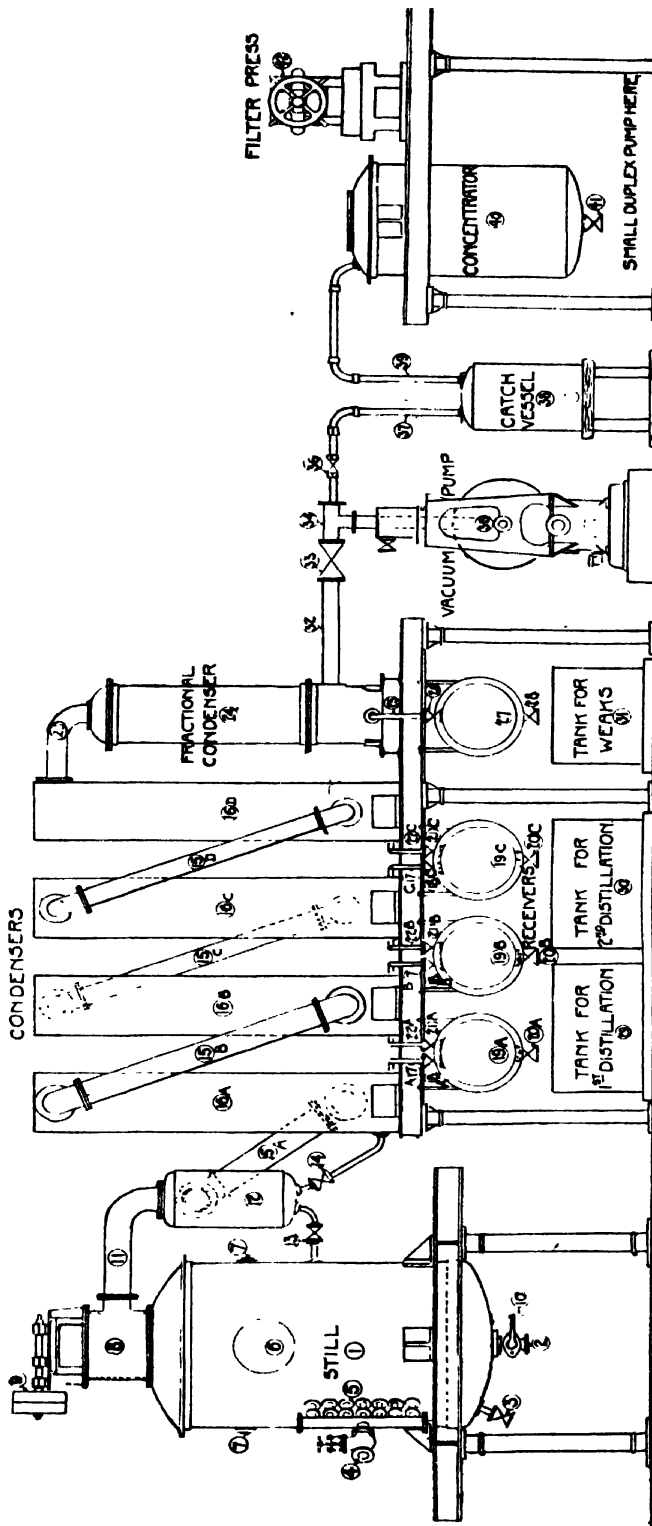


FIG. 4.—Blair, Campbell, & N'Lean's Glycerol Still.

**Van Ruymbecke and Jobbins' Process of Crude Glycerol Distillation** (see English Patents, 24,556, 1893, and 12,367, 1894).—In some of the processes of glycerol distillation explained above the glycerol still is **directly heated** below by means of a coke fire or gas (see Fig. 2), and also the steam entering the still is **directly superheated by the furnace gases**. In some of the older plants the tendency was for the contents of the still to become too hot and the steam to become superheated to such an extent that some of the glycerol was decomposed, and consequently the colour and odour of the distilled glycerol was impaired. The temperature of the superheated steam is difficult to regulate exactly, and must be made to enter at a considerably higher temperature than that at which the glycerol distils, because the steam on directly entering the vacuum of the still suddenly expands, causing a considerable lowering of temperature and thereby delaying the process of distillation.

Hence it will be seen that in order to obtain the *best results* in distilling glycerine and similar products :—

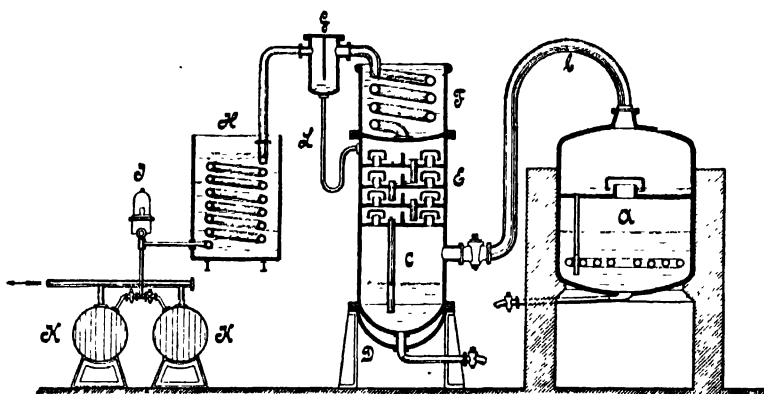


FIG. 5.—Heckmann's Glycerol Distilling Plant.

(1) The steam blowing through the still should not be superheated by direct contact with furnace gases, because it is difficult thereby to avoid the formation of decomposition products.

(2) The superheated steam should not expand *directly* into the glycerine, because by so doing it absorbs much heat and delays distillation.

(3) The still should not be heated by direct firing, but preferably by steam about  $150^{\circ}\text{C}$ . so as to avoid burning the product.

Van Ruymbecke and Jobbins (see German Patent, 86,829) avoid these difficulties as follows :—

The still A (Fig. 6) consists of a steel boiler maintained at a high vacuum of 28 in. while its contents are heated by dry steam at  $150^{\circ}\text{C}$ . circulating through closed steam coil *aa*, while at the same time a current of live steam at  $150^{\circ}\text{C}$ . is blown through the glycerol by means of an open jet *bb*. This steam enters at *c*, passes down the tube *cde*, and suddenly expands to twenty or thirty times its original volume from the narrow tube *ef* into the wide steam coil *ggg*, which is placed in the steam-heated chamber BB (felt-covered to avoid loss of heat) and which is filled with steam at  $150^{\circ}\text{C}$ .<sup>1</sup> The steam in expanding from *ef* into the wide coil *gg* has its temperature lowered, but the free steam at  $150^{\circ}\text{C}$ . in the superheater BB heats the expanded steam in the coil *gg* to its

<sup>1</sup> For higher temperatures than  $150^{\circ}\text{C}$ . the steam in BB may be replaced by hot air or a metal bath.

original temperature again, and this steam, in its expanded and dry condition, rushes through the pipe *hi* and blows in a dry hot stream through the jet *bb* into the glycerol in *AA* and causes it to distil rapidly, owing to the high vacuum maintained in *AA*, up through the pipe *CC*, into the drums *DD*, where practically pure glycerol collects ("half-refined"), while steam and the more volatile products pass away up the pipe *EE* through a series of pipes placed in a cooler *FF*, through which cold water circulates. Here the glycerol and steam are completely condensed and flow into the drum *G*, whence it is drawn off from time to time into the tank *H*. This latter distillate is known as "sweet water" and contains a small amount of glycerol and volatile organic acids. It is worked up again for pure glycerol.

The level of the glycerol in the still *AA* is maintained constant during the distillation, liquid being continually admitted slowly to maintain the level constant as

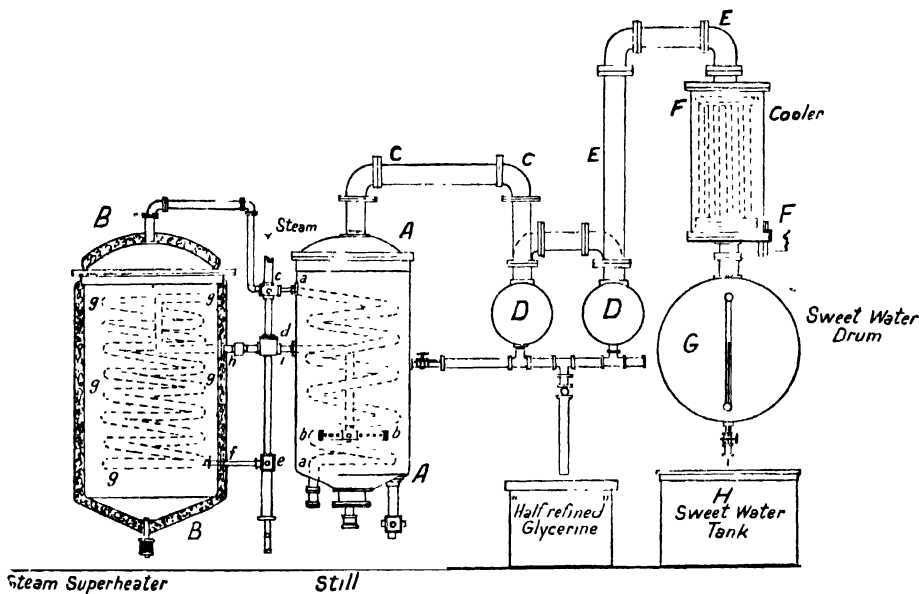


FIG. 6 — Jobbins' Glycerol Distilling Apparatus.

the liquid distils away. Finally, there remains in *A* a considerable quantity of "glycerol foots," containing 30-50 per cent. of glycerol, which is recovered from it by a special process described below.

The "half-refined" glycerol which collects in *DD* is distilled once again, and thus obtained pure and free from traces of salt which may have been carried over in the first distillation.

**Concentration and Distillation of Sweet Water.**—The sweet water contains volatile organic acids, either free or combined with glycerol. It is therefore mixed with the exact amount of soda ash to retain such acids in the "foots" as alkali salts. Next, the sweet water is placed in the steel boiler *AA* (Fig. 7), provided with a steam-heating coil *aa*; *cd* is a plate provided with a hole, at a short distance below which is another circular plate *ef* of slightly larger size, which prevents the liquid splashing up the tube *bb*, and consequently is known as the "dash plate." The valve *h* is closed, and a high vacuum is maintained in the concentrator *AA* by means of a vacuum pump connected with the receiving drum *D*. The liquid boils, water vapour passes over through *bb*, and entering the catch-all

CC, impinges against the tube *kl*, deposits the less volatile glycerol in the catch-all, while the water vapour, passing on, enters the tube *kl* and is deposited in the drum D. The glycerol deposited in CC is run back from time to time by means of *mn* into the concentrator AA.

When the glycerol in AA is sufficiently concentrated it is run into a Jobbins' distilling plant, previously described, and preferably made of tinned copper, and there finally distilled. It is finally concentrated to the proper specific gravity (1.262) and sold as "dynamite glycerol."

Refined glycerol is usually clarified by mixing a small quantity of bone-black with the hot liquid, and filtering. The product is of straw colour and is known as "dynamite glycerol." Colourless water-white glycerol is produced by a subsequent distillation and clarification of the dynamite refined grade.

Van Ruymbecke's apparatus has been introduced into many of the largest glycerol refineries in Europe and America, since it is well adapted for refining glycerol obtained either from soap-makers' lyes or from saponification glycerol (by the Twitchell process, enzyme process, or lime saponification process).

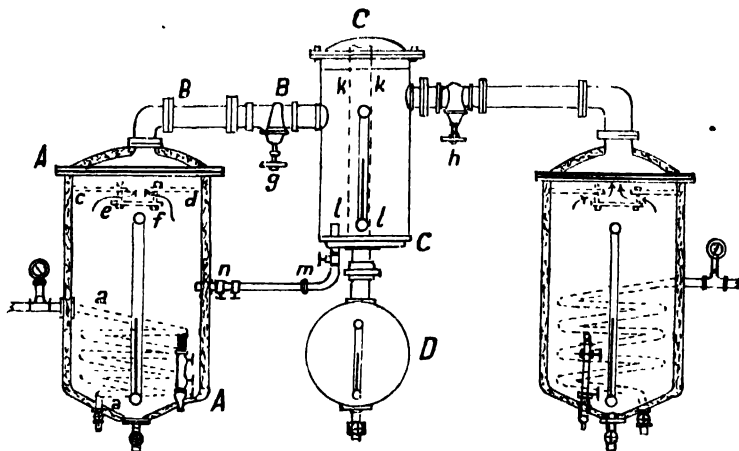


FIG. 7.—Plant for Concentrating Sweet Water.

The only defect appears to be the imperfect elimination of the volatile organic acids, like butyric acid, which distil over with the glycerol.

According to Berbeck (*Seifens. Zeit.*, 1920, 37, 44, 133, 190, 234; *Chem. Zeit.*, 1920, 44, Rep. 187), the apparatus of Van Ruymbecke (English Patents, 24,556, 1893, and 12,367, 1894) is the most suitable for distillation of impure crude glycerines and apparatus with rectifying columns for saponification glycerines. In the former method a sweet water containing 5-15 per cent. of glycerol is left, whilst in the latter the sweet water is practically free from glycerol. In Van Ruymbecke's process it is best to use steam at pressure of at least 10-14 atmospheres, so as to obtain a temperature of at least 175° C. Better rectification is effected by having the columnar vessel of the condenser in a slanting rather than in a horizontal position. In the subsequent concentration of the distillate in the receiver a temperature of 125° C. must not be exceeded and the pressure of the steam is therefore reduced to 2 atmospheres.

*E. Briggs*, in his excellent article on the distillation of glycerol, gives the following additional information as regards the working of Van Ruymbecke's plant:—

The distilled glycerol collecting in the first receiver D amounts to twice as much as collects in the second. As they become full they are emptied into condensers by opening and closing various valves, air being admitted to the receivers by opening valves at the bottom. When emptied the air valves at the bottom are closed, and connection is made with the vacuum still by very gradually opening suitable valves until the pressure is equalised.

The glycerol condensing in the first receiver possesses a sp. gr. of 1.260, and in the second receiver, 1.240. Thus the average specific gravity of the whole distillate is 1.253, representing 95 per cent. of glycerol. This is then concentrated *in vacuo* to 1.260 or 98 per cent. glycerol.

The sweet water collecting in the drum G equals the weight of the original crude charge in the still. It contains 10 per cent. of glycerol and part of the volatile impurities.

It is concentrated separately and distilled fractionally. The *foots* are treated with water and worked for more glycerol.

YIELD.—The yield is given by Briggs as follows:—Weight of crude glycerine charged to still, 149.26 cwt. at 82.8 per cent. glycerol = 123.5 cwt. glycerol.

Yield.			Cwt.	Glycerol Content.	Yield.
				Per Cent.	Per Cent
Strongs	-	-	108.5	97.5	85.7
Weaks	-	-	138	9.2	10.3
Foos	-	-	23	14.2	2.6
				Total yield	98.6
				Loss	1.4

Duration of test	-	-	-	-	42 hrs.
Vacuum	-	-	-	-	1.6 in. absolute pressure.
Steam pressure	-	-	-	-	180 lbs. per sq. in.

The fuel consumption of the Van Ruymbecke plant is 0.5 lb. coal per 1 lb. crude glycerol produced (excluding the concentration of the weaks). Assuming that the weight of the weaks is equal to the weight of glycerol fed to the still, and that 0.4 lb. of steam (=0.05 lb. coal) is required in a double effect evaporator to concentrate 1 lb. of this sweet water to 80 per cent. glycerol. The total fuel consumption is 0.55 lb. coal per 1 lb. of crude glycerol distilled. These figures include the *whole* of the steam required for the distillation (vacuum pumps, free and closed steam for still, dynamite glycerine concentrator) taken over a long period.

**Garrigue's Process for Distilling Glycerol** (see U.S. Patent, 774,172, 1904; French Patent, 349,352, 1904; English Patent, 24,100, 1904).—Fig. 8 shows a complete Garrigue's plant for glycerol distillation. A is the still in which the crude glycerol is heated to about 163° C. by a closed steam coil, while a vacuum pump H maintains a vacuum of about 28 in. Under these circumstances the glycerol rapidly distils. K is an evaporator, filled with "sweet water" from a previous distillation. This glycerol water is heated by closed steam coils in the evaporator (the steam used is low pressure direct from the exhaust of the vacuum pump H), while a vacuum of about 22 in. is maintained within the vessel. Under these circumstances the glycerol water rapidly boils, and a current of steam at a temperature considerably below 100° C. is driven along the pipe *mnoh* and rushes through a series of tubes running through the centre of a chamber C (the "superheater"), which is filled with hot glycerol vapours at about 160° C. on their way from the still A to the receiver D. Here a double action occurs. On the one hand the cooler pipes conveying the steam from K serve to condense the glycerol, while on the other hand the hotter glycerol vapours serve to heat the pipes, and consequently the sweet water vapours become greatly superheated to a temperature of about 160° C., and blow rapidly in this dry superheated condition through the perforated coil *qr* into the boiling glycerol in the still, and aids its distillation. The abstraction of heat from the vapour of the distilling glycerol where it meets the steam pipes in C causes a large part of the glycerol to condense on the tubes of the superheater, and thence drop into the first receiver D. This glycerol is a finished product, being almost water-white, with a density of 1.263. A large proportion of the glycerol vapours, however, pass on up the tube ST and enter a chamber E, called the "glycerol cooler." Through this chamber run a number of tubes conveying hot water, which, entering at a temperature of about 66° C. and leaving at about 88° C. (being heated in its passage by the hot glycerol vapours condensing on the tubes), causes the glycerol alone to condense and drop into the receiver F, while the steam passes on into the condenser G.

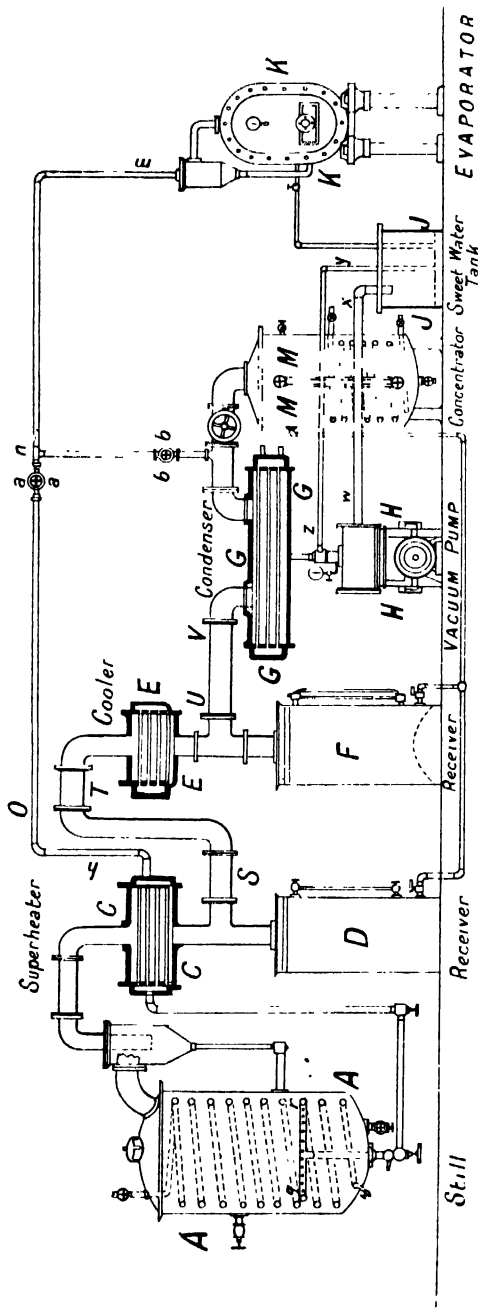


FIG. 8.—Garrigue's Plant for Distilling Glycerol.





passing through condensers maintained at such a temperature that the glycerine is condensed out, but not the steam itself. The temperature of the condensers is kept constant by means of water boiling under reduced (22 in.) pressure; moreover, the heat absorbed during the vaporisation of the glycerine is recovered during the passage through the boiling water condensers, being thereby kept within the system. In order to reduce the back pressure that would result from passing the steam by means of jets beneath the surface of the aqueous glycerine, the glycerine is pumped into the steam in the form of a fine spray, and is heated in its passage by being forced through a number of small tubes surrounded by high pressure steam. In the condensers the glycerine separates out and collects in a special receiver having an inlet and an outlet tap by means of which the glycerine can be removed without breaking the vacuum, merely by closing the inlet tap and opening the outlet tap. At the particular temperature employed the steam, which is superheated, is not condensed and passes on to the next still. As many as six stills are sometimes employed in the system, the efficiency of the last being quite equal to the first. It will be noted that the net result is to maintain in the system the latent heat of the steam employed to the last possible moment, which is rendered practicable by the fractional condensation of the glycerine vapours. The steam from the boiling water condensers is utilised to evaporate the sweet water, and also to evaporate the distilled water which provides the steam for the actual distillation.

### Other Processes

Another process of, and apparatus for, distilling glycerol is described by the *Société Française des Glycerines*, Paris (English Patent, 125,574, 7th June 1918. (Appl. 9,432/18.) Int. Conv. 16th April 1918. Addition to 123,302, 14th February 1918). In this process the crude glycerine is partially concentrated in an outer vessel at 180° C. under a vacuum of about 50 cm. of mercury, and the concentration is completed in the inner vessel at the same temperature but under a vacuum of about 72 cm. of mercury. The glycerine is drawn into the inner vessel through three atomisers by means of the difference in vacuum, or it is injected into the same by jets of steam or other gas.

**Schmidt and Joslin's Process** (U.S. Patent, 705,712, 29th July 1902).—In this process a hollow drum revolves in an outer vessel containing a shallow layer of the glycerine solution. A heating material, preferably oil, circulates through this drum from heating coils arranged in the wall of the furnace. As the drum revolves, it carries up a thin film of liquid and at the same time heats it to the distillation temperature, whilst a current of superheated steam conveys the vapour to the lowest section of a separator. The glycerine is gradually deposited in the successive chambers of the separator until eventually only steam escapes from a condenser at the top.

**Flandrak's Process** (French Patent, 318,279, 31st January 1902).—In this process the aqueous glycerine vapours are conducted through one or more condensing chambers of larger diameter than the pipe from the retort, and preferably containing iron fragments, flint particles or the like. A vessel below receives the glycerine whilst the water vapour is withdrawn from the chamber by means of the pump.

**Barbet** (French Patent, 449,961, 1912, first addition 10th June 1913) describes a still for distilling concentrated vinasse for the recovery of glycerol, where much troublesome frothing occurs. The retort is of a shallow cylindrical shape, with roof and floors bulging outwards. The floor of the retort is swept by a number of scrapers projecting downwards from two horizontal arms attached to a vertical rotating shaft.

In later patents (see English Patent, 129,649, 1919 ; U.S. Patent, 1,416,318, 1922) Barbet concentrates to a specific gravity of 1.25 in a multiple effect apparatus, dehydrates in a suitable evaporator almost completely, and then introduces the hot syrup into a column still, where, under a high vacuum, it is systematically exhausted by superheated steam, the glycerol distillate being carried over into a condenser, discharged by gravity, and concentrated. The column employed has plates with heating worms, and is provided with non-conducting or steam-jacketed walls ; the steam bubbles through the liquid in the lower part of the column, and each plate is worked by superheated steam.

The highly concentrated residue is discharged from the column under gravity through a steam-jacketed pipe to prevent premature solidification.

## CHAPTER III

# PRACTICAL DETAILS FOR MANUFACTURING DYNAMITE GLYCEROL AND CHEMICALLY PURE GLYCEROL BY THE OPEN SYSTEM OF DISTILLATION

### LITERATURE

W. E. SANGER. "Refining of Salt Crude Glycerine." *Chem. and Metall. Eng.*, vol. xxvii., No. 17, October 25, 1922.

E. BRIGGS. "The Distillation of Glycerine," article in Sidney Young's *Distillation Principles and Processes*. Macmillan, 1922.

As previously explained in the preceding chapters there are two distinct varieties of crude glycerol which are subjected to distillation, which possess different compositions, viz. :—

(a) **Crude Glycerol derived from Soap Lyes.**—*Typical analysis* (Briggs, *loc. cit.*) :—

Glycerol (T.A.V.)	-	-	-	-	-	-	81.28
Specific gravity at 20°/20° C.	-	-	-	-	-	-	1.3010
Total residue at 160° C.	-	-	-	-	-	-	12.45
Ash	-	-	-	-	-	-	9.73
Organic residue by difference	-	-	-	-	-	-	2.72
Arsenic parts per million	-	-	-	-	-	-	2.0

(b) **Saponification Glycerol** derived from the candle industry by hydrolysing fats by the *Autoclave*, *Twitchell*, or simple process.

*Typical analysis* (Briggs, *loc. cit.*) :—

Glycerol (T.A.V.)	-	-	-	-	-	86.47
Specific gravity at 20°/20° C.	-	-	-	-	-	1.2393
Total residue at 160° C.	-	-	-	-	-	0.80
Ash	-	-	-	-	-	0.42
Organic residue by difference	-	-	-	-	-	0.38
Arsenic parts per million	-	-	-	-	-	1.0

The same apparatus is used for distilling each of these products, but the larger amount of solids in crude soap lye glycerine necessitate greater precautions being taken in order to prevent overheating, and the distillation must be conducted somewhat more slowly than in the case of saponification glycerine.

It may be mentioned here that the *ash* in *crude soap lye glycerine* consists mainly of NaCl, with small amounts of Na<sub>2</sub>CO<sub>3</sub>, and oxides of iron, aluminium, and silicon derived from materials used in the preliminary treatment of the lyes. Whereas the *ash* in candle "*saponification*" glycerine usually consists of calcium or barium sulphate, which are obtained from the process of treating the "sweet water" with acid.

In both cases the organic residue consists of polyglycerols, resinous and albuminous matters, fatty acids, and the like. There is far more organic impurity in the soap lye glycerine than in the saponification.

The bulk of commercial glycerol is derived from soap lyes. With these preliminary remarks the process of distillation will be described.

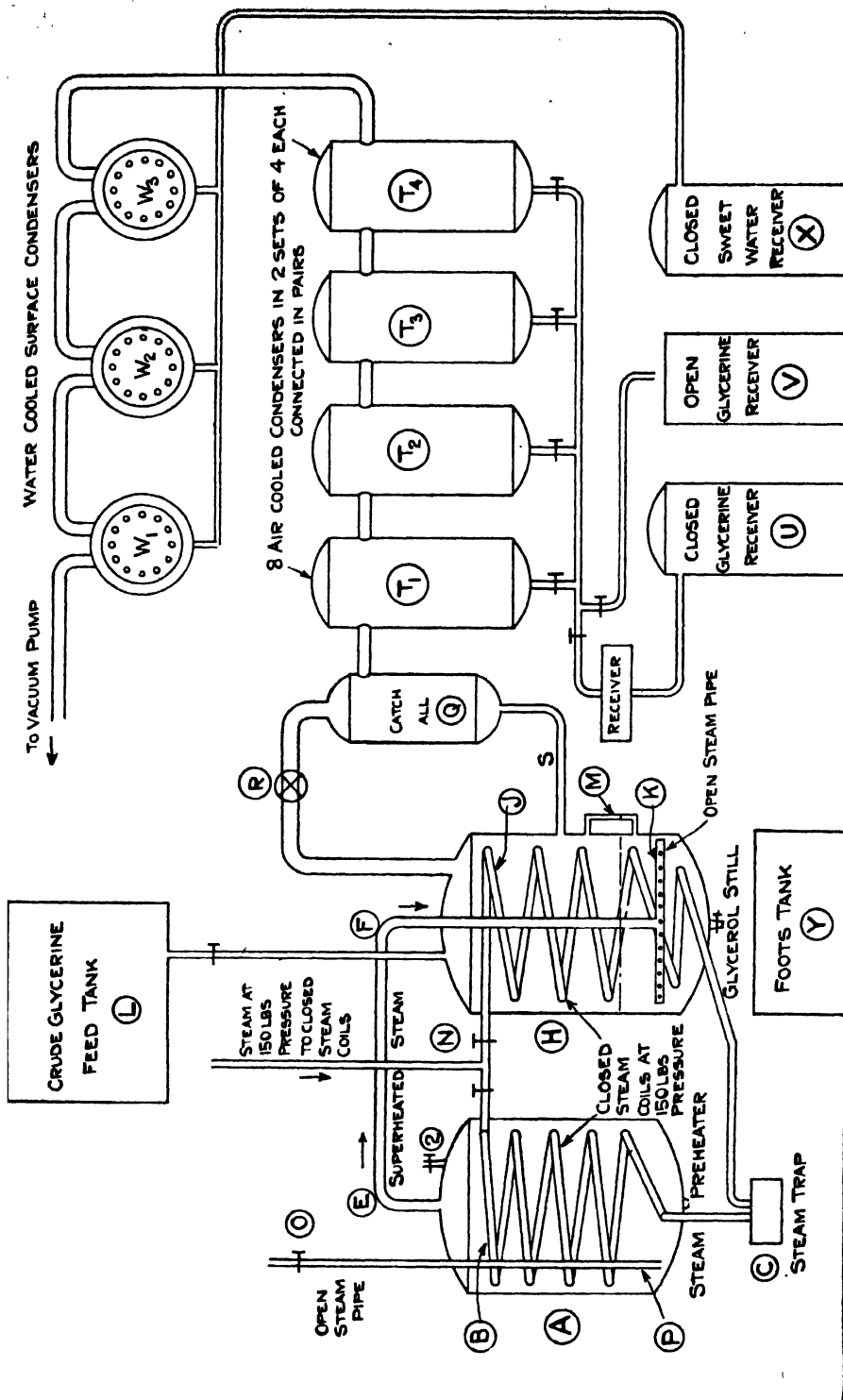


Fig. 9.—Open System of Glycerol Distillation.

As explained in the preceding chapters, in order to purify the crude glycerol it is necessary :—

- (1) To distil it.
- (2) To bleach it by charcoal or otherwise.

**Dynamite glycerol** is obtained by a single distillation and further concentration under vacuum.

**Chemically pure glycerol** requires *two* successive *distillations*, the first distillate often requiring special treatment before subjecting it to the second distillation.

**Testing the Crude Glycerol before Distillation.**—The liquid is tested for alkalinity, and sufficient caustic soda is run into the charge to give it 0.1–0.3 per cent. of free caustic soda after boiling. This is necessary to prevent frothing in the still as well as excessive amounts of volatile fatty acids in the distilled glycerol.

**Description of Plant Used in the Open System.**—This has already been described in Chapter II. (see Garrigue's plant for distilling glycerol, p. 14, Chapter II.; Jobbins' glycerol distilling apparatus, Fig. 6), but an outline of a simplified plant is shown in Fig. 9.

A is the *steam preheater*, consisting of a steel vessel A fitted with a closed steam coil extended from the top to the bottom of the straight side of the vessel and covering the bottom. The coil must be capable of withstanding over 150 lbs. pressure, and is connected to a steam trap c so that the full pressure is carried by the coil. It is important that the pressure on the coils of the system are in excess of 140 lbs., for as the pressure decreases below 140 lbs. the rate of distillation falls off very rapidly. This high pressure ensures that the preheater is kept at a sufficiently high temperature. The preheater is also fitted with a steam inlet pipe D and a steam outlet pipe E, so that the live steam thus injected into the preheater is kept superheated by the closed steam coils inside it. Hence the superheated steam from the preheater passes at an exactly controllable degree of superheat along the pipe EF into the glycerine still H.

This latter is also of steel and is fitted with a precisely similar closed steam coil J and a live steam injection pipe K, which is in the form of a perforated coil or cross on the bottom of the still.

**Starting the Still.**—The vacuum pump is put into operation so as to exhaust the whole unit.

A high vacuum on the system tends to produce a higher rate of distillation and also an improved product. There are now sold excellent vacuum pumps which will pull a vacuum on a closed suction to within  $\frac{1}{4}$  in. of the barometer.

The still is now charged with crude glycerine from the feed tank L, the liquid being drawn in either by vacuum (if the tank is on the floor level) or by gravity if the tank is elevated, as shown in the diagram. The glycerine is allowed to rise to about 10 in. on the straight side of the still, or about 4 in. in the gauge glass M.

When the vacuum has reached 25 in., steam is turned on the closed coil J, slowly opening the valve N and taking ten minutes or so to make it wide open. The object of this is to heat the still and expel any water from the crude glycerine or which was left in the still from a previous washing.

After the valve N of the closed steam coil is wide open, the valve O is turned so that a small amount of live steam passes into the preheater A via the pipe P, where it is superheated by the closed coil B.

From the preheater this live steam is drawn by the vacuum along the pipe EF and into the still H through the perforated pipe K, which is below the level of the crude in the still.

The exact quantity of steam injected varies from 1-3 lbs. per lb. of glycerine distilled, according to the quality of the crude liquor.

**Feeding the Still.**—As the distillation proceeds, more crude is fed to the still continuously in order to maintain an approximately constant level in the still, until finally the full charge of crude for the run has been fed in. A still run may vary from eight to thirty hours, the total amount of crude glycerine to be fed in before running down to “foots” depending upon the design and capacity of the apparatus.

After the full charge of crude glycerol has been fed to the still, the feed is shut off and the operation (excepting feeding crude) is continued until the foots have the desired consistency. It usually requires from two to four hours to run the foots down to “dryness” after the last of the crude glycerine has been fed.

**The Catch-All.**—The vapours from the still pass to the catch-all or separator *q*, where any entrained crude glycerol is separated from the vapours and returned to the still via the pipe *s*.

This catch-all has one vapour inlet but two vapour outlets (only one is shown in the flow sheet), one going to each set of *air-cooled condensers* *r* (of which two sets are usually employed, of four units each set, making eight condensers in all. In the flow sheet only one set is shown).

**The Air-Cooled Condensers.**—These are equipped with suitable baffle plates to cause the vapours to come in contact with the outer shells. The condensers are made of light steel plate. They are usually so connected that the condensate in each pair of condensers may be tested separately, and if the glycerol is of inferior quality it may be kept separate from the satisfactory distillate and so not contaminate it. The glycerol condensed here may be run by gravity to a closed receiving tank *u*, whence it is transferred to a storage tank previous to being concentrated to the dynamite grade in a separate concentrator.

The glycerol condensed in the first pair *T*<sub>1</sub> of air-cooled condensers is usually tested for NaCl. If it shows none of this salt, the glycerol condensed in all of the air-cooled condensers is run by gravity into the closed glycerol receiver *u*, which is under vacuum. If the sample shows the presence of NaCl, the air-cooled condensers remain shut off from the closed receiver and all glycerol is held in the condensers. At the end of the run these condensers are sampled by pairs and all glycerol giving a test for NaCl is run to the open glycerol receiver *v*, whence it is usually returned for redistillation. If the NaCl content is sufficiently low, this once distilled stock may be used for making the chemically pure grade.

The amount of distilled glycerol which is condensed in these air-cooled condensers varies considerably with the temperature of the glycerine room and is not regularly controlled by artificial refrigeration or other means. An average figure of the glycerine condensed here would be about 75 per cent. of the glycerol in the original crude.

**Sweet Water Condensers.**—The vapours which pass the air-cooled condensers go to the sweet water condensers *w*, which are of a water-cooled surface type. Here the last of the distillate vapours are condensed to form sweet water, which is run by gravity to a closed sweet water receiver *x*. From this receiver it is pumped to sweet water storage tanks.

The amount of glycerol in the sweet water will vary considerably, but allowing 5 per cent. for glycerol in the foots, this amount will be about 20 per cent. of the glycerol in the original crude glycerol.

The sweet water is drawn from the storage tanks into evaporators, where it is concentrated to sweet water crude glycerol, which is again distilled to make the dynamite grade, the residue being foots, or it may be concentrated and bleached to be sold as “yellow distilled glycerol”

The handling of yellow distilled (Y.D.) glycerol and the bleaching of the dynamite grade will be discussed later under these heads.

**Handling the Foots.**—The vapour pipe between the still and the catch-all is provided with a gate valve *R*, which permits a vacuum being pulled on the rest of the system when the still is cut off. It also prevents any foots from splashing into the catch-all when the still is being washed out.

At the end of a run the valve *R* is closed and the vacuum is then broken on the unit.

The sweet water and the dilute glycerol are run to their appointed destinations in accordance with the use to which they are to be put.

Next, the valve on the bottom of the still is opened and the hot liquid foots dropped into the tank *V*. This tank has previously placed in it some 3-4 in. of water or washings from a previous run to prevent the viscid foots adhering to the tank bottom.

**Washing Out the Still.**—After all the liquid foots have been thus removed, the valve on the still bottom is shut.

The still is provided with a pipe and a valve *Z*, which may be used as a vacuum breaker and also as a vent pipe for the steam generated in washing out the hot still.

This pipe is opened and water is slowly run into the still. Since the closed steam coil in the still possesses a temperature of about 350° F., the first lot of wash water is converted rapidly into steam, and if the wash water enters too quickly enough steam pressure may be generated to strain the joints and cause the still to leak.

Water is fed into the still to the level of 4 in. in the gauge glass, boiled for a few minutes, and then dropped into the foots tank.

A second and even a third wash is sometimes given. The works chemist estimates the glycerol contents of the various washes to see how much should be saved if the foots are to be treated for glycerol recovery. If the glycerol content falls below a certain value it does not pay to work them for glycerol and they are run to waste.

The washes which are rich enough in glycerol for working for recovery are run to the foots treatment department.

The treatment of the foots is detailed below.

**Second Distillation for Making Chemically Pure (C.P.) Glycerol (Open System of Manufacture).**—In large factories a separate distillation plant is provided for the making of chemically pure glycerol. More often, however, it is customary to use the same distillation unit for both grades. In the latter case a considerable quantity of the dynamite grade is allowed to accumulate, which is then distilled for the chemically pure product.

The first portion of the "chemically pure" glycerol which is distilled in a still used for the dynamite grade is rejected because it is contaminated with the residue of dynamite grade adhering to the walls of the condensers and tanks.

The glycerol obtained from the air-cooled condensers contains 75-90 per cent. of pure glycerol.

It is carefully analysed and may require bleaching by charcoal or acid and alkali treatment before the second distillation.

When in a correct condition for the second distillation the liquid is run into the still feed tank *L*, sufficient caustic soda added to render it slightly alkaline, and it is then distilled as described above.

**The C.P. Glycerol Foots** left in the still are returned to the salt crude tank to be distilled for *dynamite glycerol*.



The **C.P. Sweet Water** from the water-cooled surface condensers is concentrated in an evaporator to make "*c.p. sweet water crude*," which is again distilled for *c.p. glycerol*. (The residue remaining in the still from this operation becoming *c.p. foots*, and are returned to the dynamite glycerine plant.)

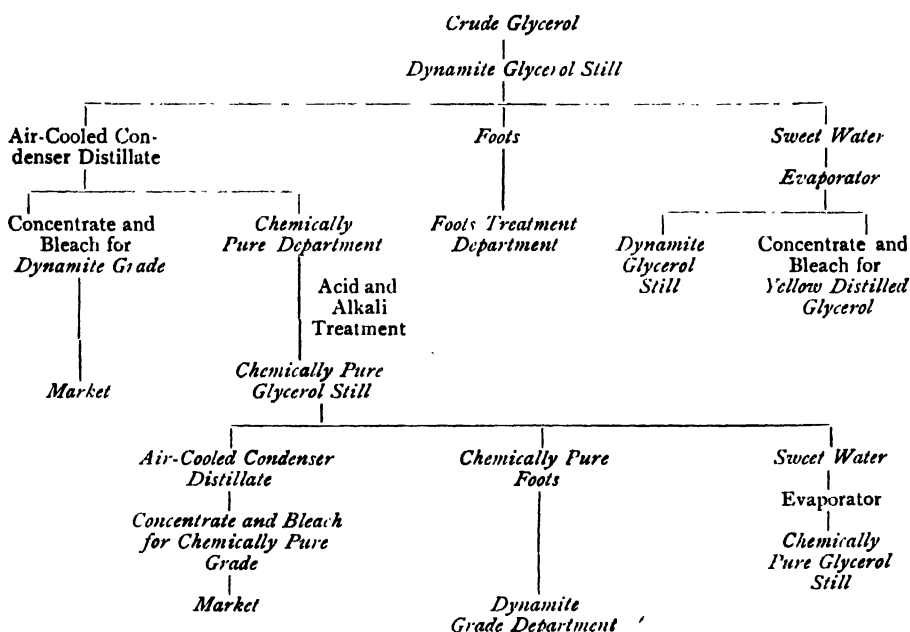
The *air-cooled condenser* product from this operation is concentrated in a *separate concentrator* and then run to the *first bleaching tanks*, where it is diluted with distilled water to give a 95 per cent. glycerol.

**Yellow Distilled Glycerol.**—Yellow distilled glycerol is a distilled glycerol which is of lower specific gravity than the dynamite grade. It is usually made by concentrating the sweet water obtained in the distillation of crude glycerol for the production of the dynamite grade, and bleaching and clarifying as described under the bleaching of the dynamite grade. It may be made by diluting the dynamite grade to a grade of lower gravity.

No standard specifications for yellow distilled glycerol are recognised, it being sold on sample, but it is usually of the same quality as dynamite glycerol but of the lower specific gravity of 29° Bé.

### Flow Chart for Distillation of Crude Soap Glycerol

The following chart enables the whole series of operations above described to be followed :—



**Elimination of Trimethylene Glycol from Glycerol.**—According to Hinckley (*Jour. Soc. Chem. Ind.*, 1907, 26, 596) trimethylene glycol gives much trouble in some plants, as it renders the glycerol unfit for dynamite making.

Its presence shows itself by the fact that even under correct temperature and vacuum conditions it is impossible to concentrate to the specific gravity specified for the dynamite grade of glycerol.

It is probably produced by the decomposition or fermentation of the fats, as it is only found where large amounts of low grade fats or kitchen grease are saponified. It also is formed when spent soap lyes ferment.

According to E. Lewis it has not been identified in modern fats but is invariably found subsequent to saponification.

It is present in a free condition in the stock, and some authorities state that it can be readily removed by giving the stock a wash preliminary to saponification. Other experts of great experience (*e.g.*, E. Lewis) dispute this assertion.

If glycol is present in the concentrated glycerine to an objectionable extent, it may be removed by distilling off a small fraction of the glycerine in the concentrator with high-pressure steam under highest vacuum. The glycol will distil more readily than glycerine, but carries glycerine off with it. By continued fractionation it is possible to produce a distillate which is high in glycol and low in glycerine.

For methods of determining the amount of *trimethylene glycol* in crude glycerine, see a paper by Cocks and Salway (*Jour. Soc. Chem. Ind.*, 1922, vol. xli., 17 T).

See also this volume, Section VI., Chapter IX.

## CHAPTER IV

## PRACTICAL DETAILS FOR MANUFACTURING DYNAMITE GLYCEROL AND CHEMICALLY PURE GLYCEROL BY THE CLOSED SYSTEM OF DISTILLATION

## LITERATURE

W. E. SANGER. "The Refining of Salt Crude Glycerine." *Chem. and Metall. Eng.*, vol. xxvii., No. 17, October 25, 1922.

**Starting the Distillation.**—A plan of the apparatus used for the closed system of glycerol distillation is shown in Fig. 10, the still being of the same general construction as that described in the preceding chapter.

A vacuum is pulled on the whole unit by the pump A.

The crude glycerol is drawn by the vacuum pump into the still B, until it stands about 10 in. on the straight side of the still or 4 in. in the gauge glass.

When the vacuum reaches 25 in. steam is turned on the extra heavy closed steam coil inside the still. As this latter covers the bottom of the still and extends up the side close to the top of the still, it effectively prevents the condensation of vapours in the still. The steam should only be turned on slowly, at least ten minutes being taken to completely open the steam valve, and the steam pressure on this coil should exceed 140 lbs. If the steam is turned on too rapidly some of the charge in the still may froth or "prime" over.

The closed steam coil is connected to a steam trap so that the full pressure may be obtained without loss of steam.

The sweet water evaporator C is filled with water to about 24 in. measured on the straight side. It is also supplied with a heating coil for generating steam to be injected into the still B.

A separate steam pipe may run to the coil inlet, or else the drain from the still coil may be by-passed to connect to the evaporator coil inlet.

The drain from the evaporator coil is also connected to a steam trap.

When the vacuum on the still B registers about 25 in., steam is turned on to the evaporator coil. Initially the still and evaporator are under about the same degree of vacuum, but as steam is generated in the evaporator, the vacuum in the evaporator drops and this steam is drawn by the higher vacuum into the still. These steam vapours pass from the evaporator C, through the preheater D (which is designed as a surface condenser) and through a perforated pipe in the bottom of the still below the level of the crude glycerol.

The crude glycerol in the still is heated to about 350° F., and a mixture of water vapours and glycerol distils over through the catch-all E, where entrained drops of crude glycerol are separated from the vapours and flow back into the still.

**Condensing the Vapours.**—From the catch-all the vapours pass through the preheater, where they pass around the tubes, while the vapours from the sweet water evaporator pass through the tubes. The water vapours generated in the

evaporator are in the form of steam under vacuum and so have a temperature of less than  $212^{\circ}$  F. The mixture of water and glycerol vapours as they pass from the still have a temperature of about  $325^{\circ}$  F. The vapours from the evaporator are thus preheated by the vapours from the still and are thus superheated before entering the still. The vapours from the still give up some of their heat in superheating the vapours from the evaporator and are thus condensed.

The glycerol vapours and the condensed glycerol pass from the preheater D to the preheater receiver E, where the vapours and glycerol are separated. The glycerol drops to the bottom of the receiver and runs by gravity to the glycerol concentrator F, which is under vacuum. The vapours pass from the preheater receiver to the glycerol cooler G.

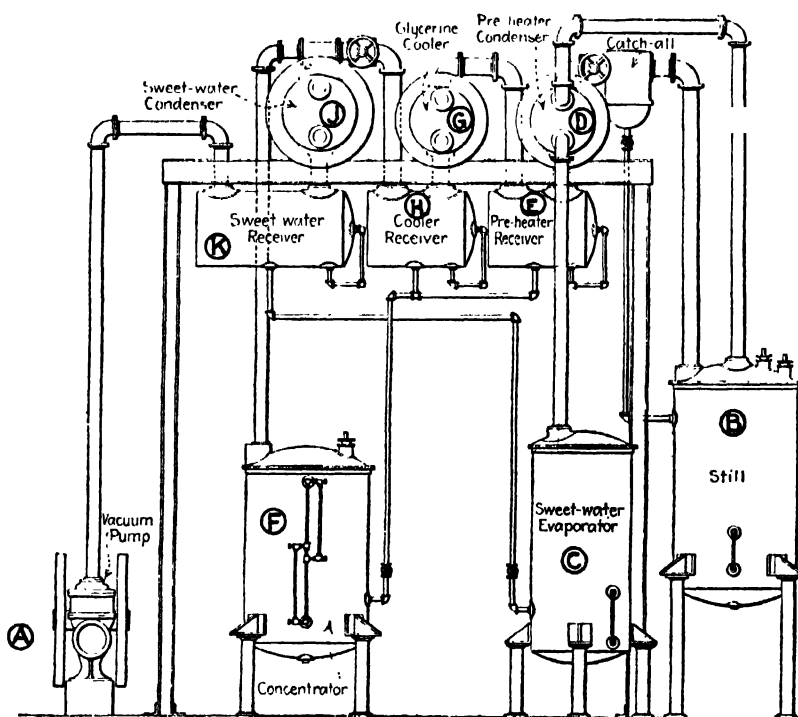


FIG. 10.—Closed System of Glycerol Distillation.

The glycerol cooler G is designed as a surface condenser, vapours passing around the tubes and water passing through the tubes for condensing purposes.

The amount and temperature of water supplied to this cooler determines the amount of glycerol which will be condensed at this point. It is possible to condense all of the glycerol in the cooler, but if this were done, the glycerol probably would not concentrate to a sufficiently high gravity for the dynamite grade due to the presence of fatty acids, esters, and glycols which are present in the distillate. For this reason the water from the cooler is run at such a temperature that most of these impurities will pass beyond the cooler and be condensed with the sweet water.

The condensed glycerol, together with the remaining glycerol vapours, passes to the cooler receiver H, where the glycerol drops to the bottom of this receiver and runs by gravity to the concentrator F. The vapours pass on to the sweet water condenser J.

One of the chief advantages of the closed system of glycerol distillation is the fact that the amount of glycerol to be condensed ready for concentration is easily controlled. In regular

practice from 90-95 per cent. of the glycerol in the original crude glycerol can be recovered in the form of dynamite grade.

The sweet water condenser J is a surface condenser wherein the vapours pass around the tubes and water passes through the tubes. All of the condensable vapours are here condensed to sweet water. The sweet water and non-condensable vapours pass into the sweet water receiver K, where the sweet water drops to the bottom and runs by gravity to the sweet water evaporator C, while the non-condensable gases pass off into the vacuum pump A.

As distillation proceeds, more crude glycerol is fed to the still in order to maintain a practically constant level. The cycle of operation is continued until a sufficient amount of crude for a run has been fed to the still.

The amount of sweet water obtained during a run is the sum of the water used in starting operations, the water present in the original crude and the glycerol, fatty acids, esters, and glycols which are condensed in the sweet water condenser. The amount of glycerol present in sweet water usually varies from 1-2 per cent. of the glycerol fed to the still in the form of crude glycerol.

**Operating the Concentrator.**—The concentrator is equipped with an extra heavy pipe coil which covers the bottom and passes part way up the straight side of this vessel. After the glycerol shows in the gauge glass on the concentrator, high-pressure steam is turned on the coil slowly so that the dilute glycerol will concentrate to the dynamite grade while the process of distillation proceeds.

After a run has been completed the concentrator, sweet water condenser, and receiver are cut off from the remainder of the distillation unit by means of a valve and the vacuum pump pulls vacuum on this part of the unit only. The vapours from the concentrator pass to the sweet water condenser. The condensable vapours are collected in the sweet water receiver, while the non-condensable vapours pass to the vacuum pump. When the charge in the concentrator reaches a temperature in excess of 350° F. under a vacuum within 1 in. of the barometer, it should be of dynamite grade. It is then transferred to the bleaching department, where a sample is taken and tested. If it is of dynamite grade, it is then bleached and drummed ready for the market. An average sample of each shipment of glycerol is analysed before shipment.

When the charge in the concentrator is finished, the vacuum is broken and the charge transferred as above described. The concentrator is not regularly washed with water.

**Difficulties caused by Impurities in the Crude Glycerol.**—If the materials used for making the crude glycerol are of low quality, or if the lyes have been stored in unclean tanks, there may be present a considerable amount of glycols and it will be impossible to obtain a glycerol of the requisite quality required for a dynamite grade.

If glycols are present to any considerable extent it will be necessary to treat the *concentrator liquid* in order to remove them.

**Concentration of the Sweet Water.**—The sweet water may be concentrated to *sweet water crude glycerol* or to *yellow distilled glycerol*, this operation being carried out in the sweet water evaporator C while running the still B down to "foots."

To do this the return pipe from the sweet water receiver K to the evaporator C is closed, so that any sweet water coming off from the still continues to collect in K while the concentration progresses in C. When the sweet water in C is sufficiently concentrated it may be redistilled for the dynamite grade, or it may be transferred to a special tank, where it is bleached and treated as described under **Yellow Distilled Glycerol**, p. 23.

**Ending the Distillation.**—When the run is completed the vacuum breaker

inlet on the sweet water evaporator is opened so that the vacuum on the still is broken through the perforated pipe at the bottom of the still.

This is to avoid drawing any still foots into the sweet water evaporator, as may easily occur if the vacuum on the still was broken before that on the evaporator.

Next, the valve on the vapour pipe beyond the catch-all is closed so that no *foots* will splash over into the preheater by this route.

Any foots getting into the preheater would be washed down by the glycerol condensing here in the succeeding run, and would so contaminate it that a second distillation would be necessary in order to produce the dynamite grade.

Finally, the vacuum breaker on the still is opened ; the foots are removed and the still washed, precisely as described in the preceding chapter.

## CHAPTER V

# DECOLORISING THE GLYCEROL BY MEANS OF CHARCOAL

**The Bleaching of Dynamite Glycerol by Charcoal.**—The dynamite glycerol as it comes from the concentrator possesses a tint which depends upon the quality of the crude glycerol from which it was distilled as well as on the design of the distilling plant.

It is therefore decolorised by bone-black as follows :—

The glycerine from the concentrator is transferred to a bleaching tank, which is equipped with an extra heavy closed steam coil for heating purposes and an open air coil for agitation. For each 1,000 lbs. of dynamite glycerine there is usually added 1 lb. of bleaching material, after which the charge is agitated for a few minutes with air. Where c.p. glycerine is manufactured, it is customary to use the spent bleach from the c.p. department for bleaching; 0.5 per cent. of charcoal is ample. Charcoal is expensive, being at the time of writing £75 per ton, and therefore economy must be exercised.

After the bleach has been added and agitated for a few minutes, the circulating pump is started. This pump takes the glycerine with bleach from the bleaching tank and delivers it to the filter press, from where it is drained back into the bleaching tank. The air is then shut off and, when necessary, steam is turned on the closed coil to maintain a temperature slightly less than 170° F. If the glycerine is permitted to become cool it is difficult to filter, and if the temperature is permitted to exceed 170° F. there is danger of precipitating colouring matter. The time required for bleaching may vary from one hour to a number of hours. Twelve hours is the usual time allowed. If it does not bleach readily, more bleach is added from time to time.

The procedure of circulating the glycerine through the press is continued until the glycerine is satisfactory as to colour and has a "shine," which is due to the removal of all solid impurities, including the bleach. When the charge is in satisfactory condition, it is drained from the press into the drumming tank, from where it is drawn off into suitable receptacles for shipment.

**The Bleaching of Chemically Pure Glycerol by Charcoal.**—The glycerol from the chemically pure concentrator should be very light in colour. The bleaching medium may be bone-black of the same kind as that used for bleaching the dynamite grade glycerol, although a higher quality must be used than for the dynamite bleach owing to more stringent specifications regarding the percentage of ash in an incinerated sample.

The glycerol from the c.p. concentrator is transferred to a bleaching tank which is equipped with an extra strong closed steam coil for heating purposes and an open coil for air agitation.

The glycerol as it comes from the concentrator has a glycerol content in excess of 95 per cent. Distilled water to reduce the content to this value is usually added so as to ensure thorough mixing of the glycerol and water.

For each 1,000 lbs. of glycerol in the tank there is added 1 lb. of bleach; it is then agitated for a few minutes and then filtered through a filter press specially reserved for this process. The filtrate is returned to the bleaching tank and the

glycerol thus circulated through the press. Samples are taken at frequent intervals, and if the bleaching is not proceeding in a satisfactory manner, more bone-black is added from time to time.

The temperature of the liquid is maintained between  $160^{\circ}$  and  $170^{\circ}$  F.

The charge is circulated through the filter press until it meets the specifications for *chemically pure glycerol*. It is then run off to drumming tanks, whence it is filled into suitable receptacles for shipment.

### Refining Crude Glycerol without Distillation by Charcoal

**Crude Lime Saponification Glycerol** is easy to decolorise by means of bone charcoal without going to the trouble of distilling it.

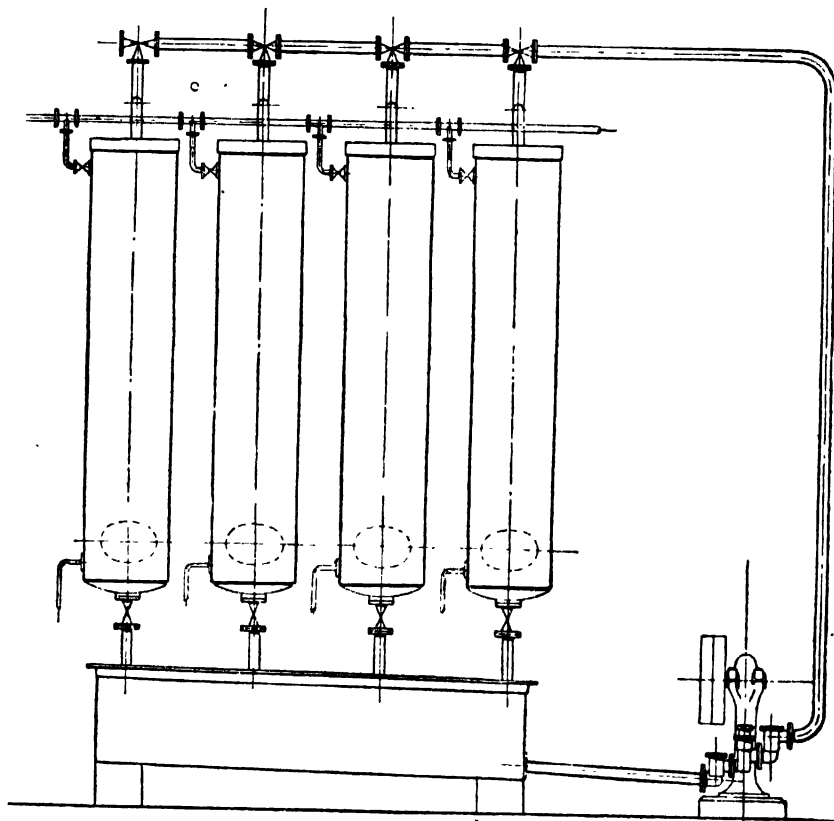


FIG. 11.—Charcoal Filters for Glycerol.

It should be noticed that neither the **crude glycerol** from soap lyes nor that produced by the **acid saponification of fats** (see pp. 3, 4, Section I) can be decolorised in this manner. Such glycerols must be distilled before they can be efficiently decolorised.

This decolorised glycerol, known as "**Commercial Refined Glycerol**," may be used technically for a number of purposes instead of distilled glycerol.

The process of decolorisation is performed as follows:—

The crude glycerine is diluted to about 50 per cent. with water ( $16^{\circ}$  Bé.) and then passed through in succession a number of cylinders filled with bone charcoal which are heated to  $80^{\circ}$  C. by means of steam coils.

Fig. 11 shows the system of charcoal cylinders, which are worked continuously, the first cylinder when exhausted being cut out of circuit, while simultaneously a freshly filled cylinder is placed in circuit at the end of the row. The crude



glycerine first comes into contact with the most exhausted cylinder and passes out through the least exhausted cylinder.

The charcoal in these filters must be regenerated. For this purpose it is well washed with water to free from glycerol (the washings being used to dilute the glycerol), then it is washed with dilute hydrochloric acid, again washed with water, then boiled with a little caustic soda, again washed with water until free from alkali, dried, placed in a closed retort in a furnace and heated to redness in absence of air (which would burn away the charcoal).

The properly regenerated charcoal is quite as effective as new.

This system of working suffers from the following defects :—

(1) Large quantities of expensive charcoal are required, which must be regenerated.

(2) The operation is slow, about five days being required for the glycerol to pass through the battery of cylinders.

(3) The glycerol, coming into contact with a large mass of charcoal, absorbs a considerable amount of calcium salts. Hence the resultant glycerol must finally be freed from these calcium salts by precipitation with sodium carbonate or sodium oxalate, heating the solution well and then filtering.

These defects may be avoided by operating as follows :—

The crude glycerol is placed in a steam-heated vessel provided with stirring gear and heated to 100° C. Small portions of decolorising charcoal are added from time to time, each addition being followed by vigorous stirring.

From 3-15 per cent. of charcoal may be sufficient, and the whole operation may be completed in an hour. Moreover, the glycerol absorbs only a small quantity of calcium salts from the charcoal, and the subsequent treatment with sodium carbonate, etc., is unnecessary.

Finally, the glycerol is freed from the charcoal by means of a filter press, and is then concentrated in a vacuum apparatus to the desired consistency.

**Remarks on Charcoal used for Decolorising Glycerol.**—The decolorising action of charcoal has been known for over a century, but the exact nature of the action is still unknown.

Some authorities regard it as an adsorption effect, depending upon the porosity and other physical condition of the charcoal.

Others consider that the nitrogen which is present in all animal charcoal and is difficult to remove, is essential to the action.

Animal charcoal must be freed from gypsum ( $\text{CaSO}_4$ ), otherwise in burning sulphur compounds may be produced which would contaminate the glycerol.

The "char" should first of all be well boiled with water, then caustic soda or sodium carbonate added until an alkaline reaction is obtained and the mass is once again well boiled. The liquor is removed and the charcoal washed with water until the washing is no longer alkaline, then treated with hydrochloric acid.

The exact procedure differs in different works, some authorities maintaining that the acid used should not be sufficient to entirely remove the calcium phosphate present, although it has been shown that this substance after exposure to heat has but a feeble decolorising effect.

The best practice is to boil the animal charcoal with four times its weight of a mixture consisting of equal parts of commercial hydrochloric acid (free from arsenic) and water for twelve hours, wash free from acid, dry and heat to redness in a closed vessel. A charcoal of great decolorising power is thus obtained.

Good decolorising charcoal possesses a dull appearance, is of a deep colour, and is best used in fine grains, not as a powder.

Exhausted charcoal from the filter presses is washed free from glycerol (which is put back in the treated lyes), purified as above described, and revived by heating in closed vessels for twelve hours.

Charcoal is only used once for high grade chemically pure glycerol. It is mainly employed for bleaching dynamite glycerine.

## CHAPTER VI

MISCELLANEOUS METHODS OF  
REFINING GLYCEROL WITH-  
OUT THE USE OF CHARCOAL

**Other Methods of Bleaching Crude Glycerol.**—The *Badische Aniline Soda Fabrik* (see German Patent, 224,394; French Patent, 410,824; English Patent, 16,260, 1909) suggests bleaching crude glycerols by means of formaldehyde-sulphoxalate.

*H. B. Stocks* (English Patent, 5,469, 1915) proposes to correct the yellow tint of partly purified glycerine by the addition of a trace of a complementary colouring matter, such as methyl or ethyl violet.

*Wislicenus* and *Bucherer* (German Patent, 202,166, 1905) suggest decolorising glycerol by means of spongy aluminium hydroxide.

**Refining Crude Glycerol without Distillation by Freezing**

In 1870 Kravt, of Hamburg, obtained pure glycerol on the commercial scale by cooling the solution of impure glycerol in leaden vessels and allowing the glycerol to crystallise out. He removed the impure mother liquors in a centrifugal machine, and thus obtained colourless crystals of M.P.  $18^{\circ}$ - $20^{\circ}$  C.

A good glycerol can be thus obtained, but it is much inferior to the best qualities produced by distillation.

The process now seems to have been abandoned.

The discovery of the crystallising power of glycerol occurred in 1867, when a cask of glycerol shipped to England from the works of Sarg & Co., at Liesing, near Vienna, arrived in England in a frozen condition.

*K. Löff* (German Patent, 314,446, 1918) modifies the process as follows :—

The solutions are treated with alcohol or other solvent for glycerol, and frozen. If, for example, a solution containing 3 per cent. of glycerol and up to 10 per cent. of mineral salts, besides proteins, carbohydrates, etc., is gradually frozen, ice crystals collect at the surface and the impurities are deposited as a precipitate. Methyl or amyl alcohol, acetone, furfural, or epichlorhydrin may be used instead of ethyl alcohol.

**Glycerol: Production of Pure.**—From liquids containing glycerol or from crude glycerol (Elektro-Osmose A.-G. (Graf. Schwerin Ges.), German Patent, 323,666, 14th February 1919). The impurities are caused to separate in flocculent form by addition of soluble silicates, preferably *water glass*, with the aid of heat if necessary. Heating may be continued until "a crystallisation skin" forms on the surface of the liquid. The products may afterwards be purified by means of lime or barium carbonate.

In *English Patent*, 144,727, 1920, a crude glycerine solution containing sulphuric acid is treated with oxalic acid, preferably in the form of a powder, and then with barium carbonate.

The addition of an amount of oxalic acid in excess of that required to precipitate the barium salt increases the bleaching action to such an extent as to avoid in some cases the necessity of adding animal charcoal.

In *English Patent*, 145,046, 1921, the addition of finely divided iron before the addition of oxalic acid is recommended.

In *English Patent*, 146,865, 1920, the glycerine is purified by electro-osmose.

An electric current is passed through the liquid, and the particles of colloids, colouring matter, and the like are carried either to the positive or negative poles.

Diaphragms are used of marked electrical potentials to assist the process.

**Glycerine : Process for the Purification of Crude.**—Vereinigte Chemische Werke A.-G., Charlottenburg (German Patent, 302,826, 19th August 1915). The glycerine is combined, in the absence of water, and if necessary in the presence of a condensing agent, with an organic acid of which the glycerol ester is insoluble in water. The ester is purified, hydrolysed, and the glycerine solution concentrated or distilled, if necessary in a vacuum.

**Glycerine : Method of Extracting.**—From distillation residues (A. Barbet, France ; addition (dated 24th January 1903) to French Patent, 323,373, 19th July 1902). A supplementary claim is made for the purification of liquids containing the crude glycerine by means of animal charcoal or chemical agents before osmosis (see *Jour. Soc. Chem. Ind.*, 1903, 502). Any other suitable solvent may be used in place of alcohol, and good results are obtained by the use of a solution of sulphur dioxide in alcohol.

## CHAPTER VII

UTILISATION OF GLYCEROL  
FOOTS RESULTING FROM THE  
DISTILLATION OF GLYCEROL

## LITERATURE

- E. LEWIS. "The Composition of the Residue on Distillation of Crude Glycerine." *Jour. Soc. Chem. Ind.*, 1922, vol. xli., 97 T.
- A. RAYNER. "Notes on the Composition of the Residue Left on Distillation of Crude Glycerine." *Jour. Soc. Chem. Ind.*, 1922, vol. xli., 224 T.
- W. E. SANGER. "Refining of Salt Crude Glycerine." *Chem. and Metall., Eng.*, vol. xxvii., October 25, 1922.

**Formation of Polymerides during the Distillation of Glycerol.**—When glycerol is distilled complex condensation products and polymerides are formed which for the most part remain behind in the still, but sometimes as much as 2 per cent. of polymerides may exist in the distilled glycerol. The formation of these polymerides occasions a serious loss in the yield of distilled glycerol.

Thus *Hepworth* (*Jour. Soc. Chem. Ind.*, 1922, 41, 100 T.) states that at Nobel's explosive works about 94 per cent. of the available glycerol was recovered, the 6 per cent. loss on 20,000 tons annually distilled being a serious loss.

The polymerisation products left behind resembled glue, and the sodium salts of organic acids accumulated in it.

Lewkowitsch states the loss incurred during the distillation of crude glycerol runs from 15-40 per cent.

Consequently attempts have been made to prevent the formation of polymerides during the operation of distilling crude glycerol.

The lower the temperature and the shorter the time of heating, the less the loss due to polymerisation. *E. Lewis* states that the amount of polymerisation was lessened by 60 per cent. in distilling crude glycerol by reducing the pressure of distillation from 30-5 mm.

Another line of attack has been the elimination of dissolved salts by strong cooling of the crude glycerol (which diminishes their solubility)

Also the effect of saturating the crude glycerol residues with hydrochloric acid gas (with a view to throwing the salts out of solution by diminishing their solubility) has been tried.

Vacuum distillation of the treated liquor showed no abnormal polymerisation.

**Treatment of Glycerol Foots from Soap Lye Glycerol.**—The "foots" comprise the tarry residue left in the still in the distilling process. They contain from 25-60 per cent. of glycerol and polymerised glycerol, 5-10 per cent. of salt, 20-30 per cent. of sodium acetate, and 10-15 per cent. of sodium salts of non-volatile fatty acids, also polyglycols. The glycerol is removed by acidifying the mass with the exact amount of sulphuric acid necessary to combine with the sodium present—the sodium being estimated in a sample by incinerating and weighing as sodium carbonate—in a lead-lined tank, and the darkened mass is, after standing, run through coarse filter canvas bags and concentrated in an iron still, when the organic acids (principally acetic) volatilise. Finally the product is added to the waste lye direct from the soap kettle and worked up along with this for glycerol

Sanger recommends the following complete method of foots treatment which may be varied to meet special conditions in any given plant :—

The foots as washed from the still are treated with a small amount of soda ash

and then filtered through a press. This treatment precipitates some of the fatty acids as sodium soap, but is primarily used to clarify the foots by removing flocculent material which is present.

The solution is run from the filter press into lead-lined tanks, where 60° sulphuric acid is added. The amount of acid to be added is determined in the laboratory, where three samples of foots are treated with varying amounts of 60° sulphuric acid in graduated glass vessels. Upon standing for a number of hours, there is a separation of tarry matter on the top and light material on the bottom. It is observed which of the three samples shows the best separation, and this is taken as the quantity to be added to the foots in the tank. The specified amount of 60° acid is added to the tank and the charge is warmed by open steam and thoroughly agitated with air. After about twenty-four hours the tarry matter, which contains considerable fatty acids, is skimmed off and discarded.

After the tarry matter has been removed the strongly acid foots are transferred to a wood vat, where they are treated to a strong alkalinity with milk of lime, which precipitates some of the remaining fatty acids. This mixture is filtered to remove the lime and lime soap, the filtrate being run to a tank, where soda ash is added to remove the excess of lime. This lime precipitate is removed in a press and the filtrate transferred to the spent soap lyes, to be again concentrated to salt crude glycerine. Where high grades of stock are used, such as in toilet soap factories, the foots may be thus returned for several years.

A simple and frequently employed method of treating foots is to transfer the foots from the still to a tank where sufficient sulphate of alumina is added to precipitate all fatty acids which can thus be removed. This solution is filtered into a second tub where sufficient acid is added to neutralise the ash alkalinity of the foots. This strong acid solution is then evaporated to foots crude glycerine.

**Yield of Glycerol from Still Residues from Distillation of Crude Glycerol.**—It is seldom possible to recover more than 50 per cent. of the glycerol contained in the foots (as estimated by the I.S.M. methods).

According to *Lach (Die Gewinnung und Verarbeitung des Glycerins, Halle, 1907)*, in Germany the average yield of glycerol on distillation of residues was 50 per cent., but in a few isolated cases a yield of 60 per cent. was obtained on prolonged distillation, but the residue was so viscous that it failed to run from the still and caused much loss of time in removal.

The **tarry residue** left in the still after the redistillation of the once-distilled glycerol is so poor in glycerol that it does not recover the latter.

Such tar is often employed in making shoe blackings, black varnishes, etc.

The **glycerol foots** resulting from the distillation of *crude glycerols low in ash*—such as Twitchell's glycerol, lime saponification glycerol and the like—are rich in polyglycerols and in salts, resulting from the accumulation of the mineral matters originally contained in the crude material.

They likewise are used in the manufacture of shoe blacking

*Claeszen* (French Patents, 392,884, 393,341) suggests using them in place of glycerine in the production of plastic masses such as printing rollers, hectograph masses, waterproofing paper, as a size for textiles, and as an ingredient for cable insulators.

*Bosse* (German Patent, 345,141, 1920) suggests manufacturing a binding agent for printing inks by precipitating impurities by the addition of salts of heavy metals or calcium earth metals.

During the war period the residues found a considerable application in Germany for the manufacture of non-freezing explosives.

The details of the methods employed have not been divulged, but a very efficient separation of chlorides and other inorganic salts must have been effected, otherwise the process of nitration would be difficult and the explosive would have been unstable.

At present it is more economical to polymerise pure glycerol, as described below in Section V., rather than purify and isolate the polymerides contained in glycerol residues.

**Osmose Treatment of Glycerine Foots.**—In a recent patent (see Elektro-Osmose A.-G. (Graf. Schwerin Ges.), English Patent, 146,865, 1920) the crude mixture is placed in the cathode compartment of a cell containing an electro-positive membrane to stop acid substances, or in the anode compartment of a cell fitted with a negative membrane to eliminate bases.

If the diaphragms are composed of electro-negative materials (*e.g.*, parchment or viscose), all basic substances pass to the cathode; whereas when the diaphragms are made of other electro-positive material, such as leather or animal membranes, all the acid constituents are eliminated.

Diaphragms of mineral matter may be used instead of organic materials, in which case an elevated temperature aids the purification.

It is stated<sup>1</sup> that in Germany during the war glycerine residues were subjected to *electro-osmosis* and thus brought into a state suitable for nitration in the manufacture of explosives, diaphragms aiding separation and acting as barriers to confine glycerol.

<sup>1</sup> E. Lewis. *Jour. Soc. Chem. Ind.*, 1922, 41, 97 T.

## SECTION III

# Miscellaneous Methods of Producing Glycerol





# CHAPTER I

## THE MANUFACTURE OF CRUDE GLYCEROL BY THE FERMENTATION OF SUGARS

### LITERATURE

- "The Manufacture of Fermentation Glycerine in Germany during the War." *Jour. Soc. Chem. Ind.*, 1919, **38**, 287 R.
- EOFF, LINDER, and BEYER. "Production of Glycerine from Sugar by Fermentation." *Jour. Ind. Eng. Chem.*, 1919, **11**, 842-845.
- A. R. LING. "Production of Glycerine from Molasses." *Jour. Soc. Chem. Ind.*, 1919, **38**, 175 R.
- "Production of Glycerine from Sugar by Fermentation." Report of the Chemistry Division of the U.S. Bureau of Internal Revenue, May 8, 1918.
- British Patents*, 138,099, 138,328, 138,330, 138,331, 1920.
- CONNSTEIN and LI DECK. *Jour. Soc. Chem. Ind.*, 1919, **38**, 691A.
- C. NEUBERG and J. HIRSCH. "Mechanism of the 'Fixation' Method of the Decomposition of Sugar into Acetaldehyde and Glycerol." *Biochem. Zeits.*, 1919, **98**, 141-159.
- C. NEUBERG and E. REINFURTH. "Alcoholic Fermentation: Correlative Formation of Acetaldehyde and Glycerol by the Scission of Sugar and New Contributions to the Theory of." *Ber.*, 1919, **52**, 1677-1703.

### INTRODUCTION

PASTEUR so long ago as 1857 proved that glycerol and succinic acid were formed in small quantities in the alcoholic fermentation of the sugars, and that consequently it occurs in wine, beer, and every other similar fermented liquor. The quantities of glycerol resulting from the fermentation vary widely; in wine it amounts to between 0.2 and 2 per cent., whereas in beer brewed with German yeasts an average of 0.6 per cent. of glycerol is found. PASTEUR obtained 3.6 g. of glycerine by fermenting 100 g. of sugar with yeast.

There is every reason to believe that the glycerine at all events formed in this way owes its origin directly to the sugars and not to the secondary constituents always present in those fermentable liquids--worts, musts, etc.--met with in commerce. In this connection it may be pointed out that F. EHRLICH showed in 1907 that the higher alcohols and esters present in fermented worts and musts are derived from the amino acids and not from the sugars. In 1909 he brought forward evidence that succinic acid is formed in the same manner.

In view of the apparent close structural relationship between the monohexoses, glucose, fructose, etc., and glycerol, the conclusion seems justified that it ought to be possible to obtain the latter compound by the fermentation of these sugars under certain conditions with one of the saccharomycetes or yeasts.

Despite numerous attempts to obtain glycerine in such quantity by the fermentation of sugars that its productions in this way would become commercially profit-

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able, no success has up to quite recently been met with, although Lüdecke obtained promising results. However, the problem of obtaining glycerine on an industrial scale by means of the fermentation of sugar assumed supreme importance in Germany after the outbreak of war, when the supplies of fat became enormously curtailed as a result of the imposition of the blockade. The extension of these researches and the conversion of the results obtained into the practical process of Connstein and Lüdecke were kept a close secret during the war, but were recently made known by Connstein at a meeting of the German Chemical Society, a report of which has appeared in the *Wochenschrift für Brauerei* (10th May 1919).

The process is based on the observation that the percentage of glycerine formed from sugar is increased if the fermentation is allowed to proceed in presence of alkaline substances. Among the latter a special position is occupied by sodium sulphite, which yeast is able to withstand in very large proportions. Thus, a solution prepared from 10 litres of water, 1 kg. of sugar, and 400 g. of the sulphite, together with ammonium sulphate, sodium phosphate, and potassium salts, is completely fermented in a few days by 100 g. of yeast.

The process was worked by the Protol Company, and as many as sixty-three factories were at first pressed into the service, although only the few largest were finally retained, the monthly output of glycerine being about 1,000 tons. Very serious practical and administrative difficulties were encountered at the outset, but these were ultimately overcome, and it was found possible to obtain 20 parts of purified glycerine, 27 parts of alcohol, and 3 parts of aldehyde from 100 parts of sugar. After removal of the yeast by filtration and of the alcohol and aldehyde by distillation, the bulk of the salts present are precipitated by calcium chloride and then by sodium carbonate, the liquid being afterwards neutralised with hydrochloric acid and filtered from the sludge formed. Concentration and subsequent distillation yield a glycerine suitable for all technical purposes. As is the case with soapworks glycerine, the distillation of fermentation glycerine is sometimes complicated by the presence of trimethylene glycol.

Neither the race of yeast, nor the nature of the sugar, nor the temperature prevailing during fermentation influences the yield of glycerine; raw sugar or even molasses is utilisable. At the termination of the fermentation the yeast exhibits certain changes in its morphological character, but still retains its fermentative capabilities; the worts used are, however, fatal to lactic and acetic bacteria.

With increase in the amount of sodium sulphite employed, the proportions of glycerol and aldehyde produced gradually increase, whilst those of alcohol and carbon dioxide continuously diminish; this is illustrated by the following experimental figures:—

Sulphite employed	-	-	-	-	25	50	100
Glycerine formed	-	-	-	-	11.3	19.6	27.1
Alcohol	-	-	-	-	40	28.7	23.3
Aldehyde	-	-	-	-	2.4	5.8	8.6
Carbon dioxide	-	-	-	-	37.6	35.8	29.4

Schweitz (*Chem. Zeit.*, 18-19, 1919) found that acid-reducing agents were unsuitable, but sodium sulphite produced a greatly augmented yield. Whereas Pasteur (1857) obtained from 100 gr. of sugar with yeast 3.6 g. of glycerine, and Oppenheimer (1914) with yeast juice got 3.12 g. Schweitzer with yeast and sodium sulphite obtained 21.3 g. The yield obtained by Eoff, Linder, and Beyer (this journal, 1919, 175 R), using a yeast and sodium carbonate, was 20-25 per cent.

**Production of Glycerol from Molasses** (see Arthur R. Ling, *Jour. Soc. Chem. Ind.*, 1919, 38, 287 R).

Dr Alonzo Taylor reported in 1917 to the United States Government that when in Germany in the summer of 1917 the Germans were producing glycerine in large quantities by a fermentation process. Investigations were undertaken at

four different laboratories in the United States with a view to elucidating the problem, and Mr A. B. Adams, Chief Chemist of the Laboratory of the Internal Revenue Bureau, Washington, was able to report to the Hon. Daniel C. Roper, Commissioner of Internal Revenue, three months after the work had been assigned to the laboratory, that Mr John R. Eoff had solved the problem in so far that he was able to produce glycerine in such quantities that if the actual cost of the recovery was not too high, the process would be commercially profitable. Details of the process have been furnished to the British and French authorities and to interested manufacturers in the United States.

The report in which the experiments are described in detail is signed by Messrs John R. Eoff, W. V. Linder, and G. F. Beyer.

After numerous trials with pure cultures of different yeasts, *Saccharomyces ellipsoideus* (var. *Steinburg*), No. 657 of the collection of the American Museum of Natural History, New York, was selected as most suitable. Preliminary experiments were then instituted which ultimately led up to the following general conclusions :—

The best yields of glycerine were obtained by fermenting solutions of sugars containing 5 per cent. of sodium carbonate, which must not be added to the liquid all at once. A less quantity of the alkali diminishes the yield of glycerine, whilst a larger quantity stops fermentation. Other alkaline substances, sodium hydroxide, potassium hydroxide, and borax may be used, but sodium carbonate (soda ash) is preferable on account of its cheapness. Although no hard and fast rule can be laid down for the method of adding the sodium carbonate, which must be varied according to the nature of the sugar solution, it should be added as soon as the fermentation has well started, and in as large quantities and as frequently as is possible without stopping fermentation. The earlier the addition of the alkali, the higher the yield of glycerine will be. It is necessary that the yeast be "worked up" by making a "bub," and it has been observed that the presence of ammonium chloride in the fermenting liquid augments the yield of glycerine. The most favourable temperature for the fermentation is 30°-32° C., and the fermenting liquid should not vary from these limits of temperature for any considerable period. Higher temperatures lead to a loss of alcohol and glycerine and to the formation of objectionable substances, whilst smaller yields of glycerine are obtained at lower temperatures. The most favourable concentration for the sugar solutions lies between 17.5 and 20 g. of sugar per 100 c.c. It has been found that when fermentation is complete, according to the method above outlined, 20-25 per cent. of the sugar originally present in the liquid is converted into glycerine, and practically all the remainder into alcohol and carbon dioxide. The nature of other substances which are formed has not yet been determined. It is mentioned that when the sodium carbonate has been added to the fermenting solution in sufficient quantity, a copious precipitate is formed, the evolution of gas ceases, and the yeast apparently lies dormant for a while. The precipitate eventually disappears and the fermentation again proceeds. It is essential that this precipitation should form, and that the fermenting liquid lie quiescent for a while. The addition of the sodium carbonate in solid form has been found to produce better results than if it be added in the form of a solution.

A description is next given of the process as carried out on a commercial scale, using inedible "black strap" Porto Rico molasses.

The yeast starter, or "bub," is first prepared in the following manner :—Yeast No. 657 (see above) was seeded with a platinum loop into 150 c.c. of sterile grape juice and allowed to ferment to the final degree. Fifteen c.c. of this was then added to 150 c.c. of sterile grape juice, and when fermentation had finished 75 c.c. was added to 800 c.c. of a solution of sterilised "black strap" molasses at 21.2° Balling (about sp. gr. 1.085). As soon as brisk fermentation had set in, 3 g. of soda ash was added and the bottle shaken until solution was complete. After fermentation had resumed, and when it had reached its final point, the whole of

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the liquid was added to 2 gals.<sup>1</sup> of a similar "black strap" molasses solution, and this was treated at the proper time with soda ash in the same proportion as before. Fermentation being complete, the whole 2 gals. was added to 40 gals. of a solution made as follows :—

"Black strap" molasses was dissolved in sufficient water to make 425 gals. of wash at 21.2° Balling at 25° C. Eight pounds of ammonium chloride was added, and after the liquid had been sterilised sufficient sterile water was added to bring it back to the original density. This solution contained 16.85 per cent. of sugar. The following are the details of the main fermentation :—

17/11/17: 9 A.M.—40 gals. of wash (see above), seeded (see above).

3 P.M.—2 lbs. soda ash added.

9.15 P.M.—The 40 gals. added to 385 gals. molasses wash.

18/11/17: 12.30 A.M.—Added 24 lbs. soda ash (T. 30° C.).

3.30 A.M.—Added 36 lbs. soda ash (T. 31.5° C.).

5.30 A.M.—Added 48 lbs. soda ash (T. 33° C. Attenuated to 30° C.)

11 A.M.—Added 48 lbs. soda ash (T. 32.5° C. Attenuated to 30° C.).

5.30 P.M.—Added 36 lbs. soda ash (T. 32° C. Attenuated to 30° C.).

The fermentation was then allowed to proceed to completion, which took five days, the temperature being kept at about 30° C.

At the conclusion of fermentation the wash was analysed and the following results were obtained:—Glycerine, 3.1 per cent. by vol.; alcohol, 6.75 per cent. by vol.; sugar (apparent), 0.86 per cent. by vol.; alkalinity, 3.6 g.  $\text{Na}_2\text{CO}_3$  per 100 c.c.

The purification of the fermented wash was then carried out as follows :—3,200 lbs. of the wash was neutralised in a tank with sulphuric acid, and 12 gals. of a saturated solution of commercial ferrous sulphate (copperas) added. The wash having been brought to near the boiling point, milk of lime was added until there was an excess of lime in solution, when the wash was boiled for half an hour by means of a steam coil. The liquid was next passed through a filter press and the cake steamed. The copperas and lime treatment was then repeated, and after again being passed through a filter press the alkalinity was brought to 0.2 per cent. ( $\text{Na}_2\text{CO}_3$ ) by the addition of soda ash. It was then filter pressed and steamed, and the filtrate evaporated in a vacuum evaporator to a thick syrup which contained between 30 and 35 per cent. of glycerine. It was then distilled in a still resembling that of Jobbin. About 50 lbs. of dynamite glycerine was thus obtained, or roughly about half that present in the fermented wash.

The following is an analysis of a sample of the dynamite glycerine :—

Specific gravity at 15.6° C., 1.2616; carbonaceous residue, 0.058 per cent.; ash, 0.009 per cent.

The carbonaceous residue is high, but a redistillation of the glycerine gave a satisfactory product. The glycerine was found to nitrate normally.

It is noteworthy that it has been found that the second treatment of the fermented wash with copperas and lime is superfluous. Hitherto it has not been found possible to obtain a perfect crude glycerine from molasses.

Several additional experiments have, it is stated, been carried out on a much larger scale (2,000 gals.) with the same results.

*Ling (loc. cit.)* comments as follows on these results :—

"It will be remembered that in an earlier part of this report it was mentioned that from 20-25 per cent. of the sugar originally present in the mash is converted into glycerine. Taking the sugars actually fermented in 'black strap' Porto Rico molasses as 50 per cent. of the molasses (and this is a very liberal estimate, for it may be computed from the figures given that nearly 3 per cent. of the sugar in the molasses is left unfermented), and remembering that only half the glycerine formed

<sup>1</sup> The gallon referred to in this article is the U.S. gallon. The factor for the conversion into British gallons is 0.834.

is recovered as crude glycerine, the yield of glycerine could not be expected to exceed  $5\frac{1}{2}$ -6 lbs. per cwt. of the molasses dealt with. It is only fair, however, to quote the following remarks of the signatories of the report. They say :—

"It must be borne in mind that there is considerable alcohol produced in these fermentations. At the present price of alcohol and raw materials it is safe to say that the value of the alcohol balances the cost of all material and overhead charges entering into the production of the fermented mash. This being true, then the slop from the alcohol distillation which contains the glycerine is free of cost, so that the only cost to be considered for the glycerine would be that of purification and distillation. This should not be great."

Experiments have also been carried out on a large scale using cane sugar and starch glucose as fermentable material. It was found, however, necessary in these cases to employ yeast foods in quantities that deleteriously influenced the purification of the glycerine. It was therefore concluded that these materials possess no superiority over molasses for the purpose.

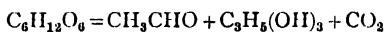
*Ling (loc. cit.)* points out that the process of producing glycerine by fermentation is in its present state of development restricted to molasses, and draws attention to the fact that in some parts of the world, notably in Australia and Fiji, molasses is a waste product which is run out to sea. He thinks, therefore, that the present process should be of great significance in such countries.

In the *Jour. Soc. Chem. Ind.*, 1919, **38**, 44 R., it is stated that in Illinois, U.S.A., a large plant for working the process has been put up. As regards the economical side it is stated, in the same place, that the price of glycerine has fallen from about 57-16 cents per lb. since the Armistice was signed, and soap-makers have said it would help them if glycerine became so cheap that they would not be required to recover it. The process of glycerol recovery comprises nearly two-thirds of their labour of manufacturing.

**Theory of the Process.**—*Neuberg and Hirsch (Biochem. Zeits., 1919, 98, 141-159)* show that at every stage during the process of fermentation of sugar in the presence of sodium sulphite, acetaldehyde and glycerol are produced in equimolecular proportions. As alcohol and carbon dioxide are also produced independently at the same time in equivalent proportions, the fermentation process can be followed by estimating the alcohol and aldehyde at the various stages.

*Neuberg* in the *Ber.*, 1919, **52**, 1677-1703, outlines the theory of formation as follows :—

Sugar is converted into methylglyoxal, which may be hydrated and reduced to glycerol or oxidised to pyruvic acid, this breaking down into carbon dioxide and acetaldehyde, which is reduced to alcohol. In the presence of sulphites the best being calcium sulphite, as is now shown, the acetaldehyde is fixed and the available hydrogen works in the direction of the production of glycerol. In fact, practically equimolecular proportions of aldehyde and glycerol are produced, and in the more concentrated solutions the quantitative realisation of the reaction



has been achieved as well as might be expected of such a biochemical process. This evidence, therefore, strongly supports the theory.

According to *Oppenheimer*, the glycerine is formed by reduction of glycer-aldehyde or dihydroxy-acetone, into which the hexoses are primarily broken up.

**Patents.**—The following patents have been published on the subject :—

**Glycerol : Manufacture of, from Sugar.**—*Vereinigte Chemische Werke A.-G.* (English Patents: (a) 138,099, 20th January 1920; and (b) 138,329, 21st January 1920. Conv.: (a) 12th April 1915; (b) 22nd April 1916). (a) Commercial sucrose, dextrose, lævulose or invert sugar is fermented by yeast in the presence of one or more organic substances of alkaline reaction, e.g., disodium phosphate, sodium or ammonium carbonate, or sodium bicarbonate. Catalysts such as manganese or iron sulphate may also be added. (b) The yeast may be

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employed for successive fermentations if after each alkaline fermentation, which is preferably conducted in presence of sodium sulphite together with a small quantity of a hydrosulphite or sulphyxylate, the yeast is regenerated by a purifying fermentation in presence of dilute acid. The yeast thus treated produces a higher yield of glycerol in each successive alkaline fermentation, and it also yields a surplus which can be used for baking or fodder. (Cf. Connstein and Lüdecke, *Jour. Soc. Chem. Ind.*, 1919, 691 A.)

**Glycerol: Manufacture of, from Sugar.**—Vereinigte Chemische Werke A.-G. (English Patent, 138,331, 21st January 1920. Conv., 18th June 1917. Addition to 138,099). In the process claimed in the chief patent and in English Patent 138,328 (*Jour. Soc. Chem. Ind.*, 1920, 608 A.), when the fermentation has attained its height a further quantity of sugar is added, if necessary, together with a small proportion of yeast and alkaline compounds, preferably sulphites, with or without other salts. This effects a considerable saving in respect of yeast, sulphite, and time.

**Glycerol: Manufacture of, from Sugar.**—Vereinigte Chemische Werke A.-G. (English Patent, 138,330, 21st January 1920. Conv., 19th May 1916. Addition to 138,099). A neutral salt of an alkaline earth metal or a magnesium or aluminium is added to the fermentation liquid. This renders possible a large increase in the amount of alkaline substance or sulphite added, and consequently an increased yield of glycerol. If 1 kg. of sugar, 500 g. of anhydrous sodium sulphite, and 250 g. of magnesium sulphate are dissolved in 5 per cent. of water and fermented at 32° C. with 100 g. of yeast, the yield of alcohol obtained is 15 per cent. and that of glycerol 33 per cent. of the weight of sugar.

See also *English Patent*, 138,328, 1920.

In *German Patent*, 343,321, 1917, an addition to the sugar is suggested of ferrous sulphate, aluminium sulphate, ammonium chloride or calcium chloride, as well as a considerable excess of nutrient salts such as ammonium sulphate, sodium phosphate, potassium sulphate, and magnesium phosphate.

A. Koch (German Patents, 331,694, 1917; 338,734, 1917) ferments sugar solutions of high concentration, e.g., 40 per cent., with large quantities of yeast, and alcohol is removed continuously by means of a vacuum or from time to time by distillation under reduced pressure.

The yield of *glycerine* amounts to at least 15 per cent. of the sugar fermented.

In the course of fermentation they may be diluted with water each time the alcohol content attains 5 per cent.

Cocking and Lilly (English Patent, 164,034, 1919) ferment sugar solutions containing mixtures of acid and normal sulphites in such proportions as to be neutral to litmus.

Yields of glycerol equivalent to nearly 50 per cent. of the sugar used were obtained.

Connstein and Lüdecke (U.S. Patent, 1,308,023, 1921) ferment sugar solutions containing soluble salts more than sufficient for the nutrition of yeast and thus convert the sugar into glycerol.

**Glycerol: Manufacture of (by Fermentation).**—J. R. Eoff, jun., Washington, U.S.A. (English Patent, 133,374, 22nd June 1918. Appl., 11,948, 1918. Int. Conv., 21st July 1917. See U.S. Patent, 1,288,398, 1918). The alkali or alkaline salt is added in successive small portions until the total amount added is just short of that which will inhibit the further activity of the yeast. The temperature during fermentation is maintained between 27° and 50° C., preferably about 37° C.

*The Industrial Alcohol Co.* (U.S. Patent, 1,423,042, 1922) recover glycerol from materials subjected to alcoholic fermentation by precipitating the organic materials with acid, distilling off the water, leaching with a liquid, and recovering the glycerine from the liquid by distillation.

*Ebers* (German Patent, 326,728, 1917) converts glycerine fermentation residues into a dry and easily extractable condition by adding common salt to the residues obtained after the bulk of the glycerol has been removed. This serves as a distributing medium, as the common salt is insoluble in alcohol or ether, which are now employed as the extracting medium for the glycerine. Slime and albuminous substances are by this process converted into forms which do not effect the extraction of the dried residues.

## CHAPTER II

# MISCELLANEOUS METHODS OF PRODUCING GLYCEROL

IN this chapter we give a few recent methods which have been proposed for producing glycerol from various sources by novel methods and which have not been discussed in the preceding pages.

**Glycerol from Distillery Residues.**—According to *L. Riviere* (*Bull. de l'Assoc. des Chim. de Sucr. et de Dist.*, 1903, **20** [10], 1043-1045), the quantity of glycerine produced as a consequence of the manufacture of two million hectolitres of commercial alcohol per annum in France is about 11.5 million kilos, the total transactions of the world in glycerine from fats being at least 60 million kilos. Instead of distilling the vinasse, the glycerine is separated as far as possible from the other constituents by an osmosis with alcohol of about 95° in a special osmogene arranged by Barbet. It is not necessary and is even disadvantageous to concentrate the vinasse too much. The mixture of alcohol and glycerine is then distilled and the aqueous glycerine concentrated to 80 per cent. of anhydrous glycerine. The vinasse from the distillation of molasses often contains 50 per cent. of substances other than glycerine, and it is then indispensable to proceed to a second osmosis to obtain saleable crude glycerine. The process may also be applied to the purification of glycerine from stearin and soap works. Such glycerines, by a single osmosis, have had their impurities reduced from 12.98-2.55 per cent.

In another patent (Glycerine, from Spent Distillation Wash: Process of Extracting: *E. A. Barbet*, French Patent, 323,373, 19th July 1902) the spent wash (vinasses), *e.g.*, from beetroot, is concentrated to 30°-40° Bé. and cooled in a current of air, after which it is mixed with 96 per cent. alcohol and subjected to osmosis. The glycerine readily passes through the parchment paper, whilst the other constituents, which are only slightly soluble in alcohol, remain behind. In this way an alcoholic liquid containing 10 per cent. of glycerine is obtained, and the residue of glycerine left after distillation of the alcohol contains only a very small amount of impurities.

Claim is also made for the simple addition of strong alcohol to the spent wash, but the glycerine carried to the surface is not so pure and the process more costly than that described above.

In a later patent, *E. A. Barbet* (French Patent, 449,961, 6th January 1912) points out that the distillation of concentrated vinasse under ordinary pressure for the recovery of glycerine is attended with troublesome frothing, and owing to the high temperature the nitrogenous organic matter decomposes and the glycerine is rendered very impure. According to the present invention, the concentrated vinasse is incorporated with a mixture of calcined plaster and some inert powder, or with a mixture of lime and kieselguhr. The mass, dried in an oven if necessary, is broken into small pieces and then packed in an iron vessel having a perforated bottom, which is placed in a still connected with an air pump and heated by hot air or steam to 200°-240° C. When the temperature of the still has been raised to about 200° C. the supply of hot air is restricted, distillation being conducted under a reduced pressure which should be as low as 60-110 mm. at the end of the operation. The distillation residue constitutes an excellent fertiliser. The crude glycerine



obtained is purified by distillation in steam under ordinary pressure, any ammonia or acetic acid which it may contain being recovered at the same time.

For the recovery of the glycerine by **distillation under reduced pressure**, *Barbet* (first addition (10th June 1913) to French Patent, 449,961, 6th January 1912) claims a **new form of retort** which permits a reduction in the amount of inert matter mixed with the vinasse to prevent frothing, so that a residue richer in nitrogen is obtained. The retort, of shallow cylindrical shape, with floor and roof bulging outwards for greater strength, is heated by direct fire with the inter-disposition of an arch of refractory material. Caramelisation of the vinasse is prevented by continuous sweepings of the floor of the retort by a number of scrapers projecting downwards from two horizontal arms attached to a vertical rotating shaft which passes upwards through a stuffing box in the centre of the roof of the retort.

In another patent (Glycerine: Extraction of, from Industrial Liquids containing it, and notably from Distillery Residues: French Patent, 344,036, 16th April 1904), *E. A. Barbet* proceeds as follows:—The liquid is concentrated to about 40°-42° Bé. and treated with powdered lime in the proportion of, say, 1-1½ kg. to 1 kg. of the syrup, from which, if necessary, crystals have been previously separated by means of a turbine. The porous mass is then treated with alcohol of as high a strength as possible (95-96 per cent.), and the alcoholic extract evaporated by means of a current of hot air or gas. The residual mass ("vinassate") from the alcoholic extraction forms a good manure. (See *Jour. Soc. Chem. Ind.*, 1903, 502; 1904, 1035.)

*Watrigant Freres et Cie* (French Patent, 445,895, 16th September 1911) (Glycerine: Extraction of, from Distillery Residues (Vinasses)) proceed as follows:—The residues are dried as completely as possible and extracted with various liquids in which the glycerine is insoluble under the conditions of the treatment, after which they are washed with hot amyl alcohol, and from this extract the dissolved glycerine separates on cooling. For example, acetone may be used in the preliminary washing to dissolve potassium malate, whilst ethyl acetate is subsequently employed to dissolve the betaine. Or ethyl acetate or a cold saturated solution of glycerine in amyl alcohol may be used to extract both potassium malate and betaine.

*G. P. Guignard and H. L. A. M. Watrigant* (English Patent, 27,300, 27th November 1912: under Int. Conv., 21st August 1912) (Extraction of Glycerine and other Useful Products contained in Distillery Vinasses) proceed as follows:—The vinasse is evaporated to dryness and treated with a quantity of sulphuric acid sufficient to liberate the organic acids, particularly malic acid, from their salts. The mass is then extracted with strong alcohol or other solvent of glycerine, and the insoluble matter, consisting mainly of sulphates and nitrogenous substances, is separated. From the soluble portion, consisting of glycerine, malic acid, and soluble nitrogenous bodies, the malic acid is precipitated as calcium malate and the alcohol is recovered by distillation. The glycerine residue is dissolved in water and employed for the treatment of further masses of vinasse until it becomes sufficiently enriched, when the glycerine is finally extracted by absorbing it in hot amyl alcohol, which is then separated from the glycerine by cooling.

*Tern* (German Patent, 357,695, 1921) suggests hydrolysing triglycerides or fats in the presence of water by the action of ultra-violet rays at ordinary temperatures and pressures.

**Glycerine from Distillers' Slops** (see *H. P. Basset*, U.S. Patent, 1,357,138, 26th October 1920: Appl., 3rd November 1919; renewed 10th September 1920).—Distillers' slop is subjected to the action of the higher hydroxide of a metal which is capable of forming higher and lower hydroxides and capable also of forming an insoluble basic salt with volatile fatty acids; the hydroxide is maintained in

the higher state of oxidation by suitable oxidising treatment ; the liquid is acidified and glycerol is separated from it.

**In Roehr's Process** (Brewers' and Distillers' Slop : Treating (Recovery of Glycerol, Dextrine, Lactic Acid, etc.): *C. J. Roehr*, Philadelphia, Pa.: U.S. Patent, 823,366, 12th June 1906) the slop is heated to a temperature of about 200° F. and treated with a solution of sodium silicate, or alkaline solutions of aluminium, zinc, copper, nickel, cobalt, or silver hydroxides. The precipitate formed is separated by means of a filter press and the filtrate evaporated to a syrup, which may be added to sizing compounds for textile purposes, dye solutions, pastes, soaps, etc.; or, if desired, the component parts of the liquid, namely, glycerol, dextrine, and lactic acid, may be separated. Partial neutralisation of the slop, before precipitation, may be effected by passing the liquid over zinc scraps.

**Lemmens and Fryer's Process.**—*G. J. Lemmens* and *P. J. Fryer* (English Patent, 126,706, 21st February 1917: Appl., 2,528, 1917) proceed as follows:—Oil or fat is subjected in an autoclave to the conjoint action of heat and pressure (about 100 lbs. per sq. in.) in the presence of an emulsifying and accelerating agent, *e.g.*, zinc oxide or hydroxide, for a lesser period than the normal time for ordinary treatment (*e.g.*, for eight hours). The strong solution of glycerine formed is withdrawn and replaced by a quantity of hot, clean, and preferably distilled water equal to about one-third to one-fourth of the weight of the original charge of oil or fat, and the treatment continued for the remainder of the usual period (*e.g.*, for four hours). The dilute glycerine obtained from the latter part of the process is drawn off and used for the initial treatment of a further charge of oil or fat.

In an earlier patent, *G. J. Lemmens* and *P. J. Fryer* (English Patent, 106,598, 21st February 1917: Appl., 2,527, 1917) proceed as follows:—Oils or fats heated in an autoclave under pressure in the presence of water and zinc oxide or zinc hydroxide, and the glycerine is recovered from the liquor in the usual way. The mixture of fatty acids and zinc soaps is treated with boiling dilute sulphuric acid, the solution of zinc sulphate is separated, the zinc precipitated as hydroxide by the addition of sodium or potassium hydroxide or ammonia, and the zinc hydroxide used in the treatment of a further quantity of oils or fats.

**Happach's Process.**—*W. Happach* and *Sudfeldt & Co.* (German Patent, 310,455, 29th November 1911) proceed as follows:—Sulpho acids of petroleum or its distillates are used as hydrolytic agents for the composition of oils and fats. For example, sulphonated petroleum hydrocarbons are separated from the deposit of uncombined tarry matter and washed with alkali solution, the uncombined hydrocarbons extracted from the soap solution by means of benzene, etc., and the purified sulpho acids liberated by the addition of an excess of sulphuric acid. From 0.5-1 per cent. is required to hydrolyse fats, and the resulting fatty acids are of better colour than those obtained by Twitchell's process.

**Budde and Robertson's Process** (Fats and Oils : Method for the Decomposition of, into Fatty Acids and Glycerine). *C. C. L. G. Budde* and *W. Robertson*, Edinburgh (English Patent, 5,715, 9th March 1909).—The oils or fats are heated and mechanically agitated with water and sulphurous acid gas, under pressure in a closed vessel or autoclave. The advantages claimed for the process are that the contents of the vessel are free from foreign matter introduced by reagents and need no purification ; that the liberated glycerine is in the form of a pure and concentrated solution ; that no permanent emulsion is formed ; and that the fatty acids are not discoloured.

**Synthetic Manufacture of Glycerol.**—*A. Heinemann* (French Patent, 458,398, 27th May 1913: under Int. Conv., 28th May 1912) proceeds as follows:—Propylene is converted into a dichloropropane by treating it with chlorine

compound, under the influence of actinic rays. The product is converted into propenyl chloride by heating it with an alkali metal, alkali compound, magnesium, etc., and this is chlorinated to form trichloropropane. On heating the latter with water, with or without an alkaline substance, glycerol is produced.

**Extraction of Glycerine in the Manufacture of "Alizarin" (Turkey-Red) Oil** (*Syndicat Internat. des Oriducteurs de Glycerine*: French Patent, 349,380, 22nd March 1904).—Claim is made for treating the castor oil with the sulphuric acid at a temperature not exceeding  $35^{\circ}$  C., at which temperature destruction of the liberated glycerine takes place. In the apparatus claimed for the process, the oil is placed in double-walled tanks of lead or other acid-resisting substance provided with hollow agitators, and the temperature is kept below  $35^{\circ}$  C. by means of leaden or other coils through which circulates a current of cold water. The Turkey-red oil is washed with water, with or without agitation, before being neutralised, etc., in the usual manner.

*Schmidt* (German Patent, 376,643, 1922) saponifies fats in the usual way, dries the product quickly, and then treats with a low boiling liquid in which dry soap is not soluble, such as acetone, methyl ethyl ketone, methyl acetate, absolute ether, etc.

The solution of glycerol so produced is separated from the undissolved matter and the solvent distilled, leaving pure *glycerol*.

*McElroy* and *The Carbide and Carbon Chemicals Co.*, in U.S. Patent, 1,466,665, 1923, propose to synthesise glycerol from petroleum oil by gasifying the latter under conditions which produce a gas rich in propylene. The gas is treated with sufficient chlorine to react with propylene, but not with ethylene. The product is recovered, submitted to further chlorination, and converted into glycerol.



## SECTION IV

# Properties, Technical Applications, and Statistics of Glycerol



## CHAPTER I

## PROPERTIES OF PURE GLYCEROL

**Properties of Pure Glycerol** ( $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$ ) or  $\text{C}_3\text{H}_5(\text{OH})_3$ .—When pure it is a solid of M.P.  $17^\circ\text{--}20^\circ\text{C}$ .<sup>1</sup> but as usually obtained it is a neutral, sweet-tasting, colourless, thick liquid of sp. gr. 1.2653 at  $15.6^\circ\text{C}$ ., which freezes to a gum-like mass when cooled to  $-40^\circ\text{C}$ ., but kept at  $0^\circ\text{C}$ . for a long time gradually solidifies, the crystals being hard and gritty.

Pure glycerol boils at  $290^\circ\text{C}$ . at atmospheric pressure. It does not volatilise at ordinary temperatures, but when heated at  $100^\circ\text{C}$ . a slight loss occurs, especially in the presence of steam.<sup>2</sup>

**Pure 100 per cent. glycerol**, placed on the skin, may raise a blister owing to its dehydrating action, while on the tongue it produces a burning sensation. Diluted with water, however, it has a softening and emolliating action on the skin, and a sweet taste.

Glycerol acts as an **antiseptic** even in diluted solution up to 12 per cent. (see Chapter II. on **Industrial Uses of Glycerol**, p. 15).

However, even a 50 per cent. solution can be fermented by various types of bacteria and yields n-butyl alcohol ( $\text{C}_4\text{H}_9\text{OH}$ ), or trimethylene glycol ( $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2\text{OH}$ ), butyric acid, lactic acid, and other products.

**Concentrated sulphuric acid** unites with glycerol, forming the compound  $\text{OH}.\text{CH}_2.\text{CH}(\text{OH}).\text{CH}_2.\text{OSO}_3\text{H}$ , which acts as an acid, forming soluble but unstable barium, calcium, and lead salts. A cold mixture of fuming **nitric** and concentrated sulphuric acid converts glycerol into glyceryl nitrate or "**nitroglycerine**,"  $\text{C}_3\text{H}_5(\text{O}.\text{NO}_2)_3$ , which finds extensive use as an explosive.

When carefully treated with dilute nitric acid glycerol is oxidised to a mixture of oxalic acid, glyceric acid ( $\text{C}_3\text{H}_6\text{O}_4$ ), and other organic acids.

Potassium dichromate and sulphuric acid oxidise glycerol completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

**Potassium permanganate**, in the presence of potassium hydroxide, oxidises glycerol to oxalic acid and carbon dioxide.

When heated with dehydrating agents such as potassium hydrogen sulphate or phosphorous pentoxide, it changes into acrolein, thus :—



Heated with small amounts of alkali, or iodine, or bicarbonate, glycerol is readily polymerised below its boiling point to **diglycerol**, and higher polymerisation products thus :—



Glycerol derived from decomposing fats frequently contains **trimethylene glycol**,  $\text{C}_3\text{H}_6(\text{OH})_2$  (or  $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2\text{OH}$ ), which lowers the boiling point and specific gravity of the glycerol and may render it unfit for dynamite manufacture owing to the unstable nature of the resulting nitrates.

<sup>1</sup> *Nitsche (Jahres. Ber., 1873, 323)* gives a M.P. of  $20^\circ\text{C}$ .; *Henninger (Ber., 1875, 8, 643)* gives  $17^\circ\text{C}$ .; *Glaque (Jour. Amer. Chem. Soc., 45, 93)* gives  $17.9^\circ\text{C}$ .

<sup>2</sup> See *Nessler and Barth (Zeit. Anal. Chem., 1884, 23, 323)*; *Clausnizer (loc. cit., 1881, 20, 58)*.

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When pure, glycerol ignites at 150° C., and burns gently with a pale blue flame without odour or residue.

The **flashpoint** of 98.9 per cent. glycerol in an open cup is 174° C., while its **firepoint** (open cup) is 187° C.<sup>1</sup>

The **specific heat** of glycerol is 0.576 from 15°-60° C. A 50 per cent. solution in water has a specific heat of 0.813.<sup>2</sup>

The **heat conductivity** calorie per second per square centimetre per 1° C. difference of temperature is 0.000637.<sup>3</sup>

The **latent heat of evaporation** is 450 B.T.U.'s per lb.<sup>4</sup>

**Latent heat of fusion** is 42.50 calories per gram.<sup>5</sup>

**Heat of combustion** is 4,323 calories per gram.<sup>6</sup>

**Electrolytic dissociation** is  $7 \times 10^{-15}$  at 14.5° C.<sup>7</sup>

**Optical rotation** is nil.

The coefficient of expansion of pure glycerol at different temperatures is given as follows :—

Temperature. ° C.	Coefficient of Cubical Expansion. (Instantaneous.)
5.0	0.0057
12.5	0.00057
15.5	0.00058
20.0	0.000612
25.0	0.000617
30.0	0.000622

Hence the mean coefficient of expansion between 15.6° and 20° C. is 0.00061, between 20° and 25° C. is 0.000615, and between 25° and 30° C. is 0.00062.

The mean coefficient of cubical expansion between 0°-100° C. is given as 0.0534.<sup>8</sup>

**Solvent Powers of Glycerol.**—At 160° C. glycerol dissolves two-thirds of its weight of boric acid, forming glyceryl borate,  $C_3H_5BO_3$ , which is used as a preservative ("boro-glyceride"). Glycerol is miscible in all proportions in water, alcohol, and aniline, sparingly soluble in ether (1,000 parts ether dissolve  $2\frac{1}{2}$  glycerol) and in ethyl acetate, 100 parts of which dissolve 9 of glycerol; glycerol is insoluble in chloroform, petroleum ether, benzene, and carbon disulphide, also in oils and fats.

Glycerol is soluble in a mixture of equal weights of chloroform and alcohol, also in a mixture of 2 vols. absolute alcohol and 1 vol. ether (which allows of its separation from sugars, dextrine, gums, and salts insoluble in such mixtures).

Glycerol also dissolves in chemically pure acetone (in which gums and salts are insoluble) and which thus serves to separate glycerol from gums and salts.

Glycerol is an excellent solvent, many substances dissolving in it with greater ease than in water or alcohol; thus it dissolves at 15° C. 98 per cent. soda crystals, 60 per cent. borax, 50.5 per cent. potassium arsenate, 50 per cent. zinc chloride, 40 per cent. alum, 40 per cent. potassium iodide, 30 per cent. copper sulphate, 25 per cent. ferrous sulphate, 25 per cent. potassium bromide, 20 per cent. lead acetate, 20 per cent. ammonium carbonate, 20 per cent. arsenious oxide, 20 per cent. arsenic acid, 20 per cent. ammonium chloride, 15 per cent. oxalic acid, 10 per cent. barium chloride, 10 per cent. copper acetate, 8 per cent. sodium bicarbonate, 7.5 per cent.

<sup>1</sup> *J. W. Lawrie*, Allan's "Commercial Analysis," 5th Edition, 1924, vol. ii., p. 738.

<sup>2</sup> *Landolt and Bornstein*, "Tabellen," 1923, vol. ii., p. 1269.

<sup>3</sup> *Loc. cit.*, p. 1303.

<sup>4</sup> *Lawrie*, Allan's "Commercial Analysis," 1924, vol. ii., p. 738.

<sup>5</sup> *Bertholet*, *Annal. Chem. Phys.* [5], 1879, 18, p. 386.

<sup>6</sup> *Landolt and Bornstein*, "Tabellen," 1923, vol. ii., p. 1593.

<sup>7</sup> *Loc. cit.*, p. 1036.

<sup>8</sup> See *Gerlach*, *Zeit. Anal. Chem.*, 24, 111; *O. Hehner*, *Jour. Soc. Chem. Ind.*, 1889, 8, 8; *Corney and Backus*, *Jour. Ind. Eng. Chem.*, 1910, 2, 11.



mercury bichloride, 5 per cent. calcium sulphite, 3.5 per cent. potassium chlorate, 1.9 per cent. iodine, 1 per cent. calcium sulphate, 0.7 per cent. iron oleate, 0.9 per cent. magnesium oleate, 1.18 per cent. calcium oleate, 0.1 per cent. sulphur, 0.25 per cent. phosphorus. Glycerol also dissolves caustic alkalis, alkaline earths, and lead oxide, and in the presence of caustic alkalis also ferric oxide, cupric oxide, and bismuth oxide.

Owing to its excellent solvent powers, glycerol when agitated with ethereal solutions of ferric chloride, ferric thiocyanate, gold chloride, and other salts, extracts them almost completely.

The presence of glycerol in aqueous solution may prevent the precipitation of mercury, copper, chromium, lead, and calcium salts, owing to the formation of soluble compounds.

**Glycerol and Water.**—Glycerol is highly *hygroscopic*, absorbing much water when exposed to damp air.

*Kailan*<sup>1</sup> (*loc. cit.*), who carried out experiments on the hygroscopicity of anhydrous glycerine and of aqueous solutions of glycerine, showed that in an atmosphere of average moisture content equilibrium is reached with a mixture of about 80 per cent. glycerol and 20 per cent. water.

When pure glycerol mixes with water and elevation of temperature takes place, which may amount to 5° C. in a mixture by weight of 50 glycerol and 42 water, simultaneously a contraction as much as 1.1 per cent. takes place. (Gerlach.)

**Specific Gravity of Pure Glycerol and Glycerol Solutions.**—The strength of glycerol solutions is usually estimated by their specific gravity, and a large number of determinations have been made of this property.

Table I. represents the table used at Nobel's explosive works (Ardeer factory), and is probably the most accurate table yet published for concentrated glycerol.

Table II. represents the current tables representing Nicol, Gerlach, Strohmmer, and Lenz's results.

Table III. gives E. Lewis's<sup>2</sup> results, showing the relation between the specific gravity and the percentage of glycerol in water solutions, the grams of glycerol per 100 c.c., and the number of cubic centimetres of pure glycerol per 100 c.c. of solutions of the different concentrations.

TABLE I

ARDEER TABLE<sup>3</sup> FOR THE PERCENTAGES OF GLYCEROL CORRESPONDING TO SPECIFIC GRAVITY AT 15.6° C.

Specific Gravity.	0	1	2	3	4	5	6	7	8	9
1.252	...	...	...	...	95.00	95.03	95.07	95.11	95.15	95.19
1.253	95.23	95.27	95.31	95.35	95.39	95.43	95.46	95.50	95.54	95.58
1.254	95.62	95.65	95.69	95.73	95.77	95.80	95.84	95.88	95.92	95.96
1.255	96.00	96.03	96.07	96.11	96.15	96.19	96.23	96.26	96.30	96.34
1.256	96.38	96.42	96.46	96.50	96.54	96.58	96.62	96.66	96.70	96.74
1.257	96.78	96.82	96.86	96.90	96.94	96.98	97.02	97.05	97.09	97.13
1.258	97.17	97.21	97.24	97.28	97.32	97.36	97.40	97.44	97.48	97.52
1.259	97.56	97.60	97.64	97.68	97.72	97.76	97.80	97.84	97.88	97.92
1.260	97.96	98.00	98.03	98.07	98.11	98.15	98.19	98.23	98.26	98.30
1.261	98.34	98.38	98.41	98.45	98.49	98.53	98.57	98.60	98.64	98.68
1.262	98.72	98.76	98.80	98.84	98.88	98.92	98.96	99.00	99.03	99.07
1.263	99.11	99.15	99.19	99.22	99.26	99.30	99.34	99.37	99.41	99.45
1.264	99.49	99.53	99.56	99.60	99.64	99.68	99.72	99.76	99.80	99.84
1.265	99.88	99.92	99.96	100.00	...	...	...	...	...	...

<sup>1</sup> A. Kailan, *Zeit. Anal. Chem.*, 1912, 51, 81, 101.

<sup>2</sup> E. Lewis, *Jour. Soc. Chem. Ind.*, 1922, 97 T.

<sup>3</sup> "Ardeer Factory Analytical Method Book," Part II. A, Method No. 33; see also *Lawrie, Allan's "Commercial Analysis,"* 5th Edition, vol. ii., p. 715.

TABLE II  
SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PURE GLYCEROL  
BY DIFFERENT OBSERVERS

Glycerol.	Nicol. <sup>1</sup>	Gerlach. <sup>2</sup>	Strohmer. <sup>3</sup>	Lenz. <sup>4</sup>	Glycerol.	Nicol. <sup>1</sup>	Gerlach. <sup>2</sup>	Strohmer. <sup>3</sup>	Lenz. <sup>4</sup>
	Specific Gravity at 20°/20° C.	Specific Gravity at 15°/15° C.	Specific Gravity at 17.5°/17.5° C.	Specific Gravity at 12-14°/12°.		Specific Gravity at 20°/20° C.	Specific Gravity at 15°/15° C.	Specific Gravity at 17.5°/17.5° C.	Specific Gravity at 12-14°/12°.
Per Cent.					Per Cent.				
100	1.26348	1.2653	1.262	1.2691	69	1.18020	...	1.179	1.1858
99	1.26091	1.2628	1.259	1.2664	68	1.17747	...	1.176	1.1826
98	1.25832	1.2602	1.257	1.2637	67	1.17474	...	1.173	1.1795
97	1.25572	1.2577	1.254	1.2610	66	1.17201	...	1.170	1.1764
96	1.25312	1.2552	1.252	1.2584	65	1.16928	1.1711	1.167	1.1733
95	1.25052	1.2527	1.249	1.2557	64	1.16654	...	1.163	1.1702
94	1.24790	1.2501	1.246	1.2531	63	1.16380	...	1.160	1.1671
93	1.24526	1.2476	1.244	1.2504	62	1.16107	...	1.157	1.1640
92	1.24259	1.2451	1.241	1.2478	61	1.15834	...	1.154	1.1610
91	1.23900	1.2426	1.239	1.2451	60	1.15561	1.1570	1.151	1.1582
90	1.23720	1.2400	1.236	1.2425	59	1.15288	...	1.149	1.1556
89	1.23449	1.2373	1.236	1.2398	58	1.15015	...	1.146	1.1530
88	1.23178	1.2346	1.231	1.2372	57	1.14742	...	1.144	1.1505
87	1.22907	1.2319	1.228	1.2345	56	1.14469	...	1.142	1.1480
86	1.22636	1.2292	1.226	1.2318	55	1.14196	1.1430	1.140	1.1455
85	1.22365	1.2265	1.223	1.2292	54	1.13923	...	1.137	1.1430
84	1.22094	1.2238	1.220	1.2265	53	1.13650	...	1.135	1.1403
83	1.21823	1.2211	1.218	1.2238	52	1.13377	...	1.133	1.1375
82	1.21552	1.2184	1.215	1.2212	51	1.13104	...	1.130	1.1348
81	1.21281	1.2157	1.213	1.2185	50	1.12831	1.1290	1.128	1.1320
80	1.21010	1.2130	1.210	1.2159	45	1.11469	1.1155	...	1.1183
79	1.20739	1.2102	1.207	1.2122	40	1.10118	1.1020	...	1.1045
78	1.20468	1.2074	1.204	1.2106	35	1.08786	1.0885	...	1.0907
77	1.20197	1.2046	1.202	1.2079	30	1.07469	1.0750	...	1.0771
76	1.19925	1.2018	1.199	1.2042	25	1.06166	1.0620	...	1.0635
75	1.19653	1.1990	1.196	1.2016	20	1.04884	1.0490	...	1.0498
74	1.19381	1.1962	1.193	1.1999	15	1.03622	...	...	1.0374
73	1.19109	1.1934	1.190	1.1973	10	1.02391	1.0245	...	1.0245
72	1.18837	1.1906	1.188	1.1945	5	1.01184	...	...	1.0123
71	1.18565	1.1878	1.185	1.1918	0	1.00000	1.00000	...	1.0000
70	1.18293	1.1850	1.182	1.1889					

H. Wolf (*Zeit. Angew. Chem.*, 1919, 32, 148) publishes a number of specific gravity determinations of extremely pure samples of glycerol. He finds that the specific gravity (referred to water at 15° C.) of a solution containing 86 per cent. of glycerine is 1.2294 at 15° C. and that of a solution containing 76.77 per cent. of glycerine is 1.2043 at 13.8° C., 1.1998 at 22° C., and 1.2036 at 15° C. The coefficient of expansion of the latter solution is 0.0004603. The results agree very closely with those contained in Gerlach's table.

A. C. Langmuir (*Jour. Ind. Eng. Chem.*, 1921, 13, 944): Very careful determinations gave sp. gr. 1.2653 at 60° F. for 100 per cent. glycerol and sp. gr. 1.2524 at 60° F. for 95 per cent. glycerol. These values reduce to 1.2655 and 1.2525 respectively for 15° C.

A. Kailan (*Zeit. Anal. Chem.*, 1912, 51, 81, 101) redetermined the specific gravity of anhydrous glycerol at temperatures between 14° and 20° C.; found values agreeing well with those found by other workers, namely, 1.26414 at 15°/4° C. and 1.26082 at 20°/4° C., and the following equation representing the relation between temperature and specific gravity was deduced:—

$$\text{Specific gravity at } t^{\circ}/4^{\circ} \text{ C.} = 1.26413 + (15 - t) 0.000632.$$

Cocks and Salway (*Jour. Soc. Chem. Ind.*, 1922, vol. xli., 18 T.) redetermined the specific gravity of standard glycerol (90 per cent.) at 20°/20° C., and gives the value 1.2378.

<sup>1</sup> Nicol, *Pharm. Jour. Trans.* [3], 1887, 18, 302.

<sup>2</sup> Gerlach, *Chem. Ind.*, 1884, 7, 277; *Zeit. Anal. Chem.*, 24, 109. Gerlach's values for 20° C./20° C. have been proved to be incorrect. See Cocks and Salway, *Jour. Soc. Chem. Ind.*, 1922, vol. xli., 19 T. Gerlach's table at 15°/15° is, however, accurate.

<sup>3</sup> Strohmer, *Monat. f. Chem.*, 5, 61; *Zeit. Anal. Chem.*, 24, 107.

<sup>4</sup> Lenz, *Zeit. Anal. Chem.*, 1880, 19, 302.

# PROPERTIES OF PURE GLYCEROL

TABLE III

PERCENTAGES OF GLYCEROL IN AQUEOUS SOLUTIONS. (E. LEWIS.)

Specific Gravity at 20°/20° C.	Grams Glycerol in 100 g.	c.c. Glycerol in 100 g.	Grams Glycerol in 100 c.c.	c.c. Glycerol in 100 c.c.
1.0117	5.00	4.94	5.06	4.09
1.0237	10.00	9.76	10.24	8.10
1.0358	15.00	14.48	15.54	12.30
1.0489	20.00	19.06	20.98	16.60
1.0610	25.00	23.56	26.53	21.00
1.0747	30.00	27.91	32.24	25.52
1.0880	35.00	32.17	38.08	30.05
1.1017	40.00	36.31	44.07	34.89
1.1150	45.00	40.36	50.17	39.72
1.1283	50.00	44.31	56.41	44.56
1.1418	55.00	48.17	62.80	49.72
1.1550	60.00	51.95	69.30	54.86
1.1691	65.00	55.59	75.99	60.16
1.1827	70.00	59.18	82.79	65.54
1.1964	75.00	62.69	89.73	71.04
1.2091	80.00	66.16	96.73	78.58
1.2237	85.00	69.46	104.01	82.35
1.2368	90.00	72.77	111.31	88.13
1.2506	95.00	75.96	118.81	94.06
1.2631	100.00	79.17	126.31	100.00

INFLUENCE OF TEMPERATURE ON THE SPECIFIC GRAVITY OF GLYCEROL SOLUTIONS OF 5-50 PER CENT. CONCENTRATION. (E. LEWIS, *Jour. Soc. Chem. Ind.*, 1922, **41**, 98 T.)

Glycerol.	15°/15°	20°/20°	25°/25°	30°/30°	35°/35°	40°/40°	45°/45°	50°/50°
Per Cent.								
5	1.0122	1.0117	1.0113	1.0108	1.0103	1.0098	1.0092	1.0087
10	1.0245	1.0237	1.0233	1.0227	1.0221	1.0215	1.0209	1.0203
15	1.0370	1.0358	1.0354	1.0350	1.0346	1.0340	1.0334	1.0328
20	1.0495	1.0489	1.0481	1.0474	1.0467	1.0460	1.0453	1.0446
25	1.0621	1.0610	1.0605	1.0600	1.0593	1.0586	1.0579	1.0572
30	1.0753	1.0747	1.0737	1.0729	1.0721	1.0713	1.0705	1.0697
35	1.0885	1.0880	1.0869	1.0861	1.0853	1.0845	1.0837	1.0829
40	1.1023	1.1017	1.0905	1.0896	1.0887	1.0878	1.0969	1.0960
45	1.1156	1.1150	1.1142	1.1134	1.1125	1.1116	1.1106	1.1095
50	1.1290	1.1283	1.1274	1.1263	1.1253	1.1240	1.1229	1.1220

## 8 THE MODERN SOAP AND DETERGENT INDUSTRY

**Refractive Index of Pure Glycerol and Glycerol Solutions.**—A very important and rapid check on the purity of glycerol solutions is their refractive index.

*Lenz*<sup>1</sup> gives the following table :—

TABLE OF THE REFRACTIVE INDEX,  $N_D$ , AT 12.5°-12 8° C. OF  
AQUEOUS SOLUTIONS OF GLYCEROL. (LENZ.)

Glycerol.	N <sub>D</sub> .	Glycerol.	Glycerol.	N <sub>D</sub> .	Glycerol.	N <sub>D</sub> .	
Per Cent.		Per Cent.	Per Cent.		Per Cent.		
100	1.4758	74	1.4380	49	1.3993	24	1.3639
99	1.4744	73	1.4366	48	1.3979	23	1.3626
98	1.4729	72	1.4352	47	1.3964	22	1.3612
97	1.4715	71	1.4337	46	1.3950	21	1.3599
96	1.4700	70	1.4321	45	1.3935	20	1.3585
95	1.4686	69	1.4304	44	1.3921	19	1.3572
94	1.4671	68	1.4286	43	1.3906	18	1.3559
93	1.4657	67	1.4267	42	1.3890	17	1.3546
92	1.4642	66	1.4249	41	1.3875	16	1.3533
91	1.4628	65	1.4231	40	1.3860	15	1.3520
90	1.4613	64	1.4213	39	1.3844	14	1.3507
89	1.4598	63	1.4195	38	1.3829	13	1.3494
87	1.4569	62	1.4176	37	1.3813	12	1.3480
86	1.4555	61	1.4158	36	1.3798	11	1.3467
85	1.4540	60	1.4140	35	1.3785	10	1.3454
84	1.4525	59	1.4126	34	1.3772	9	1.3442
83	1.4511	58	1.4114	33	1.3758	8	1.3430
82	1.4496	57	1.4102	32	1.3745	7	1.3417
81	1.4482	56	1.4091	31	1.3732	6	1.3405
80	1.4467	55	1.4079	30	1.3719	5	1.3392
79	1.4453	54	1.4065	29	1.3706	4	1.3380
78	1.4438	53	1.4051	28	1.3692	3	1.3367
77	1.4424	52	1.4036	27	1.3679	2	1.3355
76	1.4409	51	1.4022	26	1.3666	1	1.3348
75	1.4395	50	1.4007	25	1.3652	0	1.3330

*H. Wolf* (*Zeit. Angew. Chem.*, 1919, 32, 148) gives the following values :—86 per cent. solution  $N_D = 21.4545$  at 12.5°, 1.4537 at 15°, and 1.4533 at 17.5° C.; 76.72 per cent. solution, 1.4401 at 12.5°, 1.43945 at 15°, and 1.4388 at 17.5° C. The change in refractive index per 1° C. was  $2.8 \times 10^{-4}$  for the 86 per cent. solution and  $2.6 \times 10^{-4}$  for the 76.72 per cent. solution.

In order to determine rapidly the percentage of glycerol in a solution, the refractive index may be taken. In order to avoid the necessity of maintaining a known constant temperature and of accurately estimating the zero error of the refractometer used, *Lenz* advises that the refractive index of the glycerol solution and of pure water be observed successively. The following table gives the *differences* between the refractive index of water and of aqueous solutions of glycerol of various concentrations :—

<sup>1</sup> *Lenz, Zeit. Anal. Chem.*, 1880, 19, 297

TABLE OF DIFFERENCES BETWEEN REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF GLYCEROL AND OF PURE WATER ( $N_D$  SOLUTION— $N_D$  WATER), AFTER LENZ

Glycerol.	Difference.	Glycerol.	Difference.	Glycerol.	Difference.	Glycerol.	Difference.
Per Cent.		Per Cent.		Per Cent.		Per Cent.	
100	0.1424	75	0.1061	50	0.0663	25	0.0318
99	0.1410	74	0.1046	49	0.0659	24	0.0315
98	0.1395	73	0.1032	48	0.0645	23	0.0302
97	0.1381	72	0.1018	47	0.0630	22	0.0288
96	0.1366	71	0.1003	46	0.0616	21	0.0275
95	0.1352	70	0.0987	45	0.0601	20	0.0261
94	0.1337	69	0.0970	44	0.0587	19	0.0238
93	0.1323	68	0.0952	43	0.0572	18	0.0225
92	0.1308	67	0.0933	42	0.0550	17	0.0212
91	0.1294	66	0.0915	41	0.0541	16	0.0190
90	0.1279	65	0.0897	40	0.0526	15	0.0186
89	0.1264	64	0.0889	39	0.0510	14	0.0173
88	0.1250	63	0.0861	38	0.0495	13	0.0160
87	0.1235	62	0.0842	37	0.0479	12	0.0146
86	0.1221	61	0.0824	36	0.0464	11	0.0133
85	0.1206	60	0.0806	35	0.0451	10	0.0120
84	0.1191	59	0.0792	34	0.0438	9	0.0108
83	0.1177	58	0.0780	33	0.0424	8	0.0096
82	0.1162	57	0.0768	32	0.0411	7	0.0083
81	0.1148	56	0.0757	31	0.0398	6	0.0071
80	0.1133	55	0.0745	30	0.0385	5	0.0058
79	0.1119	54	0.0731	29	0.0372	4	0.0046
78	0.1104	53	0.0717	28	0.0358	3	0.0033
77	0.1090	52	0.0702	27	0.0345	2	0.0021
76	0.1075	51	0.0688	26	0.0332	1	0.0008

**Boiling Points of Pure Glycerol and Glycerol Solutions.**—Pure glycerol boils at  $290^{\circ}$  C. at 760 mm. Hg. with slight decomposition.

If the glycerol contains even traces of certain salts the decomposition on boiling at ordinary pressures may become noticeable, acrolein as well as polyglycerides and water being produced.

The influence of a trace of moisture in reducing the boiling point of glycerol is remarkable.

Thus pure glycerol boils at  $290^{\circ}$  C. (760 mm.), but even 0.04 per cent. of moisture lowered the boiling point to  $283^{\circ}$  C., while 1 per cent. moisture lowered the boiling point from  $290^{\circ}$ – $224^{\circ}$  C. (760 mm.). (See Grun and Wirth, *Zeit. Angew. Chem.*, 1919, 32, 59.)

The boiling points of pure glycerol under reduced pressures are as follows :— $210^{\circ}$  C. at 50 mm. Hg. ;  $192^{\circ}$  C. at  $30^{\circ}$  C. ;  $179.5^{\circ}$  C. at 12.5 mm. Hg. ;  $163^{\circ}$  C. at 10 mm. Hg. ; and  $143^{\circ}$  C. at 0.2 mm. Hg.<sup>1</sup>

The following table of the boiling points of aqueous solutions of glycerol has been published by E. Lewis.<sup>2</sup>

Other tables have been given by Grun and Wirth<sup>3</sup> (which agrees closely with Lewis's values) and by Gerlach,<sup>4</sup> which differs somewhat from the values of the two more recent investigators.

<sup>1</sup> See Mendelejeff, *Annal. Chem. Phys.*, 1860, 16, 114-117 ; Boles, *Trans. Chem. Soc.*, 1871, 9, 84 ; Richardson, *Jour. Chem. Soc.*, 1886, 49, 764 ; Kailan, *Zeit. Anal. Chem.*, 51, 83.

<sup>2</sup> E. Lewis, *Jour. Soc. Chem. Ind.*, 1922, 41, 991.

<sup>3</sup> Grun and Wirth, *Zeit. Angew. Chem.*, 1919, 32, 59.

<sup>4</sup> Gerlach, *Chem. Ind.*, 1884, 7, 277.

**BOILING POINTS OF AQUEOUS SOLUTIONS OF GLYCEROL AT  
760 MM. PRESSURE. (E. LEWIS.)**

Glycerol.	° C.	Glycerol.	° C.	Glycerol.	° C.
Per Cent.		Per Cent.		Per Cent.	
100	290.0	90	137.5	40	104.2
99	225.5	85	126.8	35	103.5
98	196.0	80	121.5	30	103.0
97	179.5	75	116.5	25	102.4
96	168.0	70	113.5	20	102.0
95	160.0	65	111.0	15	101.5
94	156.0	60	108.8	10	101.0
93	149.5	55	107.2	5	100.5
92	145.5	50	106.0	...	...
91	141.0	45	105.5	...	...

**Viscosity of Pure Glycerol and Glycerol Solutions.**—J. Kellner (*Z. deuts. Oet u. Fettind.*, 1920, **40**, 677-678) recommends viscosity measurements as a value test for the purity of glycerol.

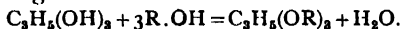
He gives tables in the original paper which the reader should consult.

The viscosity of aqueous solutions of glycerol at 20° C. are given in the following table<sup>1</sup> :—

**VISCOSITY OF GLYCEROL SOLUTIONS AT 20° C. (ARCHBUTT AND DEELEY.)**

Glycerol.	Density Grams per c.c. of Glycerol.	Viscosity C.G.S. Units.	Viscosity Kine- mater C.G.S. Units.
Per Cent.			
5	1.0098	0.01181	0.01170
10	1.0217	0.01364	0.01335
15	1.0337	0.01580	0.01529
20	1.0461	0.01846	0.01765
25	1.0720	0.02585	0.02411
35	1.0855	0.03115	0.02780
40	1.0989	0.03791	0.03450
45	1.1124	0.04692	0.04218
50	1.1258	0.05908	0.05248
55	1.1393	0.07664	0.06727
60	1.1528	0.1031	0.08943
65	1.1797	0.2149	0.1822
75	1.1932	0.3371	0.2825
80	1.2066	0.5534	0.4586
85	1.2201	1.025	0.8401
90	1.2335	2.076	1.683
95	1.2465	4.801	3.852

**Compounds of Glycerol.**—*Glycerol* unites with a large number of metallic hydroxides to form soluble compounds called *glyceroxides*, which are formed according to the following scheme :—



The mono-, di-, and tri-sodium glyceroxides have been prepared in the pure state, so also have been the calcium, barium, mono-lead, and various mixed metallic glyceroxides.

<sup>1</sup> The table is taken from *Archbutt's and Deeley's* "Lubrication and Lubricants," 1st Edition, pp. 161-164, who recalculated the values given by *Schöttner* (*Sitzber. d. Kaiserl. Akad. d. Wissenschaften Wien*, 1878, **77**, 682; 1879, **79**). See also *Landolt and Bornstein*, "Tabellen," 1922, vol i., 130, 186, where full references are given to the extensive literature.

The formation of such compounds is the reason why glycerol prevents the precipitation from solution by alkalis of mercury, chromium, and copper salts.

The alkaline-earth and lead oxide compounds are soluble in water and not decomposed by carbonic acid. In the presence of alkali hydroxide such heavy metallic oxides such as cupric oxide, ferric oxide, and bismuth oxide are dissolved by glycerol. Complex double compounds, called *glycerinates* (see *Grün and Bockisch, Ber.*, 1908, 3465), are formed with copper sulphate, cobalt sulphate, nickel sulphate, etc.

**Glyceryl Phosphoric Acid**,  $C_3H_5(OH)_2O.PO(OH)_2$ .—Formed by mixing  $P_2O_5$  with glycerol, and known only in aqueous solution (20-50 per cent.). Dibasic acid. Salts used medicinally, having a strong action on the nervous system. In this form phosphorus is rapidly assimilated. **Tonal** is the name given to preparations of its salts, **kalio-tonal** being potassium glyceryl phosphate.

For the constitution of glyceryl phosphoric acid see *Power and Tulin, Trans. Chem. Soc.*, 1905, 87, 249; *Tulin and Hann, Trans. Chem. Soc.*, 1906, 89, 1749.

For the estimation of **glycero-phosphates** see *A. Astruc, Jour. Pharm.*, 1898 [6], 7, 5; *A. Trillat, ibid.*, 163; *Imbert and Pages, ibid.*, 378.

*Merck and Weber* (German Patent, 331,695, 1920) make a double salt of glycero-phosphoric acid and lactic acid.

*Stephan* (German Patent, 339,537, 1919) prepares water soluble glycero-phosphates of iron and albumen.

The trade in glycero-phosphates is considerable. The imports of *glycero-phosphates* into Great Britain were:—

Year.	Weight. Lbs.	Value. £
1920 - - - - -	39,375	13,994
1921 - - - - -	9,853	3,891
1922 - - - - -	15,898	1,252

The exports were:—

Year.	Weight. Lbs.	Value. £
1920 - - - - -	3,729	1,913
1921 - - - - -	1,977	616
1922 - - - - -	3,497	933

**Arsenic Compound of Glycerol**.—Large quantities of arsenious oxide are dissolved by glycerol to form **glyceryl arsenite**  $C_3H_5AsO_3$ , which has been employed by calico printers for fixing aniline colours. It forms an amber-yellow, fatty substance, M.P.  $50^\circ C$ . Soluble in glycerol and water; excess of water is said to decompose it. But E. Lewis states that he has found it extremely difficult to decompose glycerol arsenites even in steam.

Arsenic sometimes occurs in soap-lye glycerol which has been neutralised by crude hydrochloric acid, owing to the fact that it volatilises (probably in the form of a volatile compound) when glycerol is distilled.

Hence glycerol is difficult to purify from arsenic once the latter has been introduced.

Attempts have been made to oxidise the arsenites to arsenates and hence make a more stable compound which will not volatilise from the still.

According to *J. Galimard and E. Verdier (J. Pharm. Chim.*, 1906, 23, 183-184), it is found that although the so-called "pure" glycerols of commerce fail to give any indication of arsenic by the Marsh test when introduced direct into the testing apparatus, the same samples, after being boiled for ten hours under a reflux condenser, with an equal volume of water acidified with 1 per cent. of pure sulphuric acid, invariably give a distinct arsenical ring when so tested. It is evident, therefore, that glycerol may contain an arsenical impurity which is not reduced by the ordinary procedure of Marsh's test. Probably the arsenic is present as an ester, which requires the treatment indicated to render its presence evident. All the samples of "pure" glycerol examined gave indications of arsenical contamination. See also *Sand and Hackford's* work on the "Oxidation and Reduction of Arsenic Compounds."

**Glyceryl Borate**,  $C_3H_5BO_3$ , is formed by heating three parts of glycerol at  $160^\circ C$ . with two parts of boric acid.

It has been used as an antiseptic under the trade name of "*boroglyceride*."

See, however, *R. Dubrisay, Comptes Rend.*, 1921, 172, 1658-1660, who maintains that boric acid and glycerol do not form a compound.

## CHAPTER II

# TECHNICAL APPLICATIONS OF GLYCEROL

**Uses of Glycerol.**—By far the greater part of glycerol is used for making nitroglycerine; besides this it is used as a sweet conserving fluid for preserved fruit, as a lotion or basis for ointments in toilet soaps, in gas meters, and hydraulic jacks to prevent freezing, for lubricating moulds, for preventing shrinkage in wooden vessels, in clay modelling, in artists' colours, in calico printing, in cements and inks, in photography, to impart elasticity to leather and paper, etc. Glycerol is sometimes (illegally) added to alcoholic drinks as an unfermentable and harmless sweetener.

Glycerol is used in the manufacture of formic acid, allyl alcohol, and artificial mustard oil. It is also used as a solvent in extracting perfumes and alkaloids due to its high solvent action. A brief account of some of the uses will prove interesting. The manufacture of nitroglycerol is described in the author's work, "Nitrogen Products and Explosives," and will not be further referred to.

**Lead Glyceride (Glycerol Cement).**—When glycerol is mixed with litharge ( $\text{PbO}$ ) a mass is obtained which after a time becomes of stone-like hardness and forms the basis of a series of very resistant cements.

According to Morawski, a definite union occurs between the litharge and the glycerol, the body having the composition  $\text{C}_3\text{H}_5(\text{HPbO}_3) + \text{H}_2\text{O}$ , which can be obtained in the form of crystalline needles if glycerol is added to a solution of the litharge in caustic potash.

A mixture of 50 g. litharge and 5 c.c. of glycerol yields the most solid cement, but it sets rather too rapidly. It is easier to mix 5 vols. of glycerol with 2 vols. of water and then mix 60 c.c. of the mixture with 50 g. of litharge. After ten minutes the mass is fairly hard, and after three hours harder than any other.

A harder and more solid cement is made by mixing 10 vols. of glycerol with 4 vols. of water and then mixing 6 c.c. of this solution with 50 c.c. of lead oxide. After two hours the mass is quite solid.

Glycerine cement is a yellowish or brownish composition, which when pressed into moulds and allowed to harden for some days fills out the finest hollowings in the mould, and consequently has been used for making coin impressions.

The cement maintains its elastic properties, and consequently has often been used for making the foundation of stamping machines and steam engines.

It is also used for cementing stones together. The stones are pasted with glycerol, litharge powdered over the mass, and the surface then pressed together and kept some days under pressure.

**Use of Glycerol as a Softening Substance.**—Glycerol evaporates extremely slowly (owing to its high boiling point) and, moreover, is extremely hygroscopic. Consequently a substance (like a skin) which has become hard and dry on exposure to the air will, when mixed with glycerol, keep moist and supple. Moreover, the glycerol, being antiseptic in nature, will prevent decay. The antiseptic effect is more pronounced if previously salicylic acid or boric acid be dissolved in the glycerol.



Hence glycerol finds application for the preservation of furs, stuffed animals, and animal skins. It is better than alcohol for preserving specimens of marine animals, etc., which shrink and lose their colour in alcohol but not in glycerol.

An excellent preserving liquor consists of glycerol 200 g., water 400 g., and salicylic acid 4 g. Formaldehyde may be substituted for the salicylic acid.

Instead of using "degras" for oiling chamois leather, glycerol may be used instead. When leather belting is impregnated with glycerol it is rendered soft and pliable, so that it runs around the pulley wheels without undue consumption of power.

A similar small scale application of glycerol is its use in preparing microscopic objects for examination.

In the **paper trade** the brittleness of paper made from straw and wood pulp is diminished by the addition of a small amount of glycerol to the paper pulp.

**Wood**, carefully dried in a kiln at 70°-80° C. and impregnated with glycerol, can be bent without cracking.

**Casks** impregnated with glycerol keep damp because glycerol is a water-attracting substance; the glycerol also arrests the development of fungi, etc., in the casks on account of its antiseptic properties.

**Glycerol-Glue Preparations.**—When glycerol and glue or gelatine are melted together on cooling, a firm jelly-like mass is produced which receives extended application for printing rollers, hectographic blocks and the like. Simple recipes are: (1) glue, 1 part; glycerol at 28° Bé., 5 parts; (2) glue, 1 part; glycerol at 28° Bé., 4 parts; water, 1 part.

Occasionally barium sulphate, kaolin, etc., are added to the mass, but their use is doubtful.

**Glycerol-Gelatine** is widely used for embedding microscopic specimens for examination.

**Gelatine Capsules** and **Court Plaster** contain glycerol.

*G. Diesser* (German Patent, 358,540, 1915) grinds egg- or blood-albumin with glycerine, yielding liquid products which rapidly harden either alone or on treatment with formaldehyde or potassium bichromate. The products are suitable for making moulded articles, for use as an adhesive for cellulose, waste leather, or cork, or for adding to rubber.

*Claessen* (German Patent, 198,711, 1907) proposes using the viscous mixtures of **diglycerine** and **polyglycerines** prepared by heating glycerine for the preparation of finishing materials and plastic substances, e.g., a finish for cotton and linen consists of 30 parts cologne size, 45 parts water, 35 parts starch syrup, and 5 parts of polyglycerine. A waterproof gelatine paper is made by coating the paper on both sides with a solution of 1 part gelatine, 0.25 part polyglycerine, and 4 parts of water, and drying it.

**Artificial Resins from Glycerol.**—Another recently developed field for the use of glycerol is in the production of *artificial resins*.

Thus *Downs* and *Weisberg* (British Patent, 173,225, 1920) produces a resin by heating a polyhydric alcohol (such as glycerol) with a polybasic aliphatic acid or anhydride, such as *fumaric*, *maleic*, etc.

A sticky mass is produced which on cooling solidifies to a fusible solid.

On further heating, this turns into an infusible mass insoluble in acetone, and on still more highly heating gives rise to a resin insoluble in acetone and other organic solvents, resistant to cold and boiling water and acids at ordinary temperatures, but decomposed by hot caustic soda.

A series of patents have been taken out by the *General Electric Co.* (U.S.A.) for making similar resins using succinic and phthalic acids and anhydrides.

## THE MODERN SOAP AND DETERGENT INDUSTRY

**Use of Glycerol in Making Hectographic and Copying Inks.**—In a good hectographic ink the colouring matter must be very intense and the ink must never dry up. Warm glycerol has the property of dissolving many powerful aniline dyes and also does not dry up. Consequently it enters into the constitution of many of the best inks of this type.

For the same reasons glycerol is employed in the manufacture of copying inks.

**Blackening** for boots sometimes contains glycerol.

**Uses of Glycerol as a Solvent.**—The remarkable solvent properties of glycerol cause it to be very widely used in the arts.

The capacity of dissolving aniline dyes is taken advantage of in the printing and dyeing trades, where glycerol is often substituted for alcohol with advantage.

Glycerol has also been used for extracting perfumes from flowers, for the extraction of pepsin and other medicinal preparations from organic tissues, etc.

In the United States the use of glycerol for *flavouring extracts* has considerably increased since the prohibition laws have restricted the use of ethyl alcohol.

**Use of Glycerol in Cosmetics.**—Glycerol finds a very extensive use in the preparation of cosmetics. In the words of a well-known writer on cosmetics:—

“If properly applied it possesses the quality of imparting to the skin brilliance softness, and delicate colour.”

A skin which has been tanned by the sun is very rapidly bleached by the application of dilute glycerol. Apparently the glycerol penetrates into the tissue and dissolves the deposited colouring matter, so that on washing away the glycerol the colouring matter is removed with it. The colour of moles and freckles is similarly abstracted by glycerol.

Full particulars of such cosmetic preparations must be sought in works devoted to that subject.

The glycerol must be applied diluted with water. In concentrated form the glycerol abstracts water from the skin and may injure the tissues.

**Use of Glycerol in the Manufacture of Toilet Soaps.**—The cosmetic effects of glycerol, referred to in the preceding section, are widely employed in the manufacture of toilet soaps. Glycerol is directly added to the soap.

It has the further effect of transmitting transparency in the soap, and in causing it to yield a good lather and rapidly dissolve in water.

For particulars the reader should consult the author's work on “Soaps.”

**Uses of Glycerol in Medicine.**—Glycerol finds a wide application in medicine owing to its softening action on the skin and on account of its great solvent power, e.g., “**glycerol plaster**” consists of a paste of starch with glycerol, which may form the vehicle for introducing various medicinal preparations into the skin.

It also enters into the preparation of numerous salves and “chilblain cures,” and into the constitution of the numerous soaps used for medicinal purposes, e.g. **liquid tar soaps** (potassium oleate + alcohol + glycerol + water + tar), **liquid storax soap**, and **liquid antiseptic soaps**.

Glycerol is also used in the preparation of *lymph* for vaccination, for the extraction of pepsin, for keeping moist pill and tablet masses, for court plaster and gelatine capsules, for liniments, salves, and injections, for earache and skin diseases, etc.

**Use of Glycerol for the Manufacture of Pharmaceutical Preparations.**—A considerable amount of glycerol is used in the manufacture of *glycero-phosphates*. “Glyceryl-phosphoric acid” or “glycero-phosphoric acid” is obtained

## TECHNICAL APPLICATIONS OF GLYCEROL

by heating glycerol with *phosphoric acid*. This forms the basis of many so-called "brain foods."

*Glycerol borates* (boro-glyceride), *phenolates*, *tannates*, and *arsenites* are also manufactured, the boron compound being used as a preservative.

**Use of Glycerol as an Antiseptic.**—*G. Seiffert* and *A. Spiegl* (*Zentr. Bakt.*, 1914 [1], 74, 518; *Chem. Zeit.*, 1915, 39, Rep. 306) used glycerol as a sterilising medium. All the micro-organisms examined, viz., *B. coli*, *Paratyphus B.*, *B. pyocyaneus*, *V. Metschnikoff*, *B. diphtheria*, *Staphylococcus albus*, *Streptococcus brevis*, *B. anthracis*, and *B. subtilis*, were killed in one minute by heating with glycerine at 120° C. Sterilisation by heating with glycerine is specially suitable for porcelain filters, rubber tubing, and surgical instruments; the latter are not injured and do not rust even when kept in the hot glycerine for one hour.

*Kreucher* (*Hygien. Rundsch.*, 1908, 18, 313-330), who points out that *Warington* first discovered the antiseptic power of glycerol in 1846, shows that warming glycerol with bacteria to 35°-37° C. soon kills the latter.

*O. von Wunschheim* (*Arch. Hyg.*, 39, 101-141; *Chem. Centr.*, 1901, 1 [7], 408) shows that commercial glycerine exerts a certain bactericidal influence on *Staphylococcus pyogenes aureus* and *B. coli*. In mixtures of glycerine and water, the bacteria can exist for the longest time when the proportion of water is large: the effect of mixtures containing small proportions of water appears to vary according to the kind of bacteria used. Sulphuric acid, oxalic acid, caustic potash, phenol and three isomeric cresols, creolin, saprol, lysol, thymol, formol, and tannin possess less disinfecting power when dissolved in glycerine than in aqueous solution of equal concentration. On the other hand, hydrochloric acid and acetone are more active in glycerine solution than in aqueous solution, whilst acetic acid has about the same disinfecting power with both solvents. The disinfecting power of aqueous glycerine solutions, containing 2.5 per cent. of phenol, increases, the greater the proportion of water present, and with a solution containing about 50 per cent. of water is equal to that of a 2.5 per cent. aqueous solution of phenol. Phenol, o-cresol, lysol, and creolin possess less disinfecting power in glycerine soap solutions than in aqueous soap solutions of the same strength.

*H. P. Goodrich* (*Brit. Med. Jour.*, 1907, 647; *Pharm. Jour.*, 1917, 98, 453) pointed out that glycerine impairs the antiseptic power of thymol, phenol, boric acid, and mercuric chloride in aqueous solution. Many antiseptics, inorganic as well as organic, are much more soluble in glycerine than in water. For example, the approximate solubilities percentages at ordinary temperatures of the following substances in water and glycerine respectively are: Thymol, 0.06, 0.526; phenol, 7.7, 350.0; mercuric chloride, 5.26, 61.5; boric acid, 4.0, 25.0. In a mixture of equal volumes of water and glycerine about five times as much thymol will dissolve as in plain water, but the resulting solution has no better antiseptic power than the aqueous solution containing only a fraction of the amount of thymol. The same applies to boric acid; a saturated solution in water will kill all the organisms on a thin film of *Staphylococcus pyogenes aureus* in just over an hour, whereas a saturated solution in water and glycerine containing more than four times as much boric acid requires about six hours. It has long been assumed that solutions in glycerine were more antiseptic than the weaker aqueous solution, but it is a fact that even water compares well in disinfecting power with 50 per cent. glycerine. Pure glycerine easily kills protozoa, but it is by virtue of its osmotic action. Dilute solutions are not even preservative. A 3.3 per cent. solution of phenol in water destroyed all the individuals in a standard culture of *S. pyogenes aureus* contained on a thin film on a cover glass in less than a quarter of a minute; the same strength solution in water and glycerine required more than a minute. The comparative figures for mercuric chloride (0.005 per cent. solution) are  $\frac{1}{2}$  and  $\frac{1}{2}$  minute; for boric acid (saturated aqueous solution, i.e., 4 per cent.), 65 minutes; half-saturated solution, 12 $\frac{1}{2}$  minutes; 2 per

cent. solution in water and glycerine more than 480 minutes; thymol (saturated solution),  $\frac{1}{4}$  minute; half-saturated solution (0.03 per cent.),  $12\frac{1}{2}$  minutes; same strength in glycerine and water, more than 300 minutes.

**Addition of Glycerol to Wine, Beer, and Liqueurs and Foodstuffs.**—Modern law has prohibited the addition of glycerol to wines, beers, and liqueurs. Formerly it was the practice to add small amounts of glycerol to acid wines, as thereby a soft sweet taste was imparted and the glycerol, on standing, partially united with the acids, thereby rendering the taste "smoother."

The addition of glycerol to beer renders it sweeter in taste and allows it to retain the froth for a much longer time.

In **liqueurs** glycerol was added as a partial substitute for sugar.

Anyone at present adding glycerol to natural beverages such as the above renders themselves liable to prosecution.

**Glycerol** is also put into lemonade and liqueurs, punch essence, sweetmeats, and chocolates (to prevent them drying up), in **fruit** preservation, for albumen and egg yolk preservation, in vinegar, mustard, and for preserving meat.

**Glycerol for Filling Gas Meters.**—The liquor in gas meters consists of glycerol diluted to 45 per cent. of water. The meters are thus prevented from freezing and from drying up, since in the course of twelve months some 10-15 per cent. of water is absorbed from the gas by the glycerol. Nevertheless, the liquor should be renewed once a year, the glycerol purified by heating to  $130^{\circ}$  C. for some hours, until all alkaline reaction has ceased, decolorising with charcoal and filtering, and used over again.

**Glycerol for Filling Motor Car Radiators.**—During 1925 much glycerol was sold in the United States for filling motor car radiators. The glycerol keeps the water from freezing and also does not evaporate sensibly.

The *Standard Oil Co.* of New York patents the use of a stable *foam* containing a large amount of glycerol that is employed to prevent evaporation of gasoline, etc., from large oil tanks.

**Glycerol for Clay Modelling.**—When clay is prepared by sculptors for modelling by the use of a liquid composed of 1 part of glycerol dissolved in 3 parts of water, a plastic mass is obtained which does not crack on drying or shrink as does clay prepared with water alone.

**Use of Glycerol in the Manufacture of Tobacco.**—Glycerol is often added to snuff and chewing tobacco, in order to keep them moist, sweet to the taste, and act as a partial antiseptic.

This is probably the second largest use of glycerol, the main outlet being its use for the manufacture of nitroglycerine.

**Use of Glycerol in the Weaving Industry.**—Glycerol has been applied to weaving for keeping the threads of cotton moist in the weaving of fine muslin. One well-known dressing used for this purpose consists of glycerol 14, water 30, alum 1, dextrine 1. The glycerol which enters into the fabric gives it an increased degree of suppleness and elasticity.

# CHAPTER III

## STATISTICS RELATING TO GLYCEROL

ACCORDING to *Davis (Jour. Soc. Chem. Ind., 1900, 19, p. 112)*, in 1890 the world's production of glycerol was 40,000 tons, of which 26,000 tons were produced in stearin manufacture and 14,000 tons from spent soap lyes. Great Britain's share was 5,500 tons, while the United States produced 3,000 tons by stearin and 3,000 tons by soap lyes.

By 1910 the world's production of glycerol amounted to about 80,000 tons, and of this quantity *Great Britain* produced about 25,000 tons crude glycerol per annum from soap lyes and 500-600 tons from stearin.

In 1921 one single firm (Nobel's Explosive Company) distilled 20,000 tons of glycerol per annum.<sup>1</sup>

The *imports* and *exports* of glycerol into Great Britain are as follows :—

### Imports OF GLYCEROL INTO GREAT BRITAIN

	Crude.	Value.	Distilled.	Value.
	Cwts.	£	Cwts.	£
1909	51,959	111,404	10,045	30,595
1910	67,258	179,970	11,806	49,990
1911	105,961	308,998	16,350	75,260
1912	112,764	303,065	22,902	91,421
1913	87,908	255,718	22,076	84,570
1914	85,293	258,200	15,613	65,769
1915	95,755	272,029	40,813	165,862
1916	32,393	101,007	22,970	104,144
1917	7,900	43,518	15,831	128,824
1918	63,490	491,404	29,785	376,937
1919	40,759	363,933	784	10,729
1920	24,140	111,435	9,676	56,029
1921	32,544	118,517	3,808	19,543
1922	43,821	109,841	5,363	23,249
1923	24,660	...	3,800	...

<sup>1</sup> *Hepworth, Jour. Soc. Chem. Ind., 1922, 41, 100 T.*



## SECTION V

# Polymerised Glycerol and Glycerol Substitutes





# CHAPTER I

## MANUFACTURE, PROPERTIES, AND ESTIMATION OF POLY- MERISED GLYCEROL

### LITERATURE

E. LEWIS. *Jour. Soc. Chem. Ind.*, 1922, **41**, 97 T.

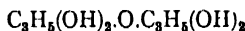
A. RAYNER. *Jour. Soc. Chem. Ind.*, 1922, **41**, 224 T. Also patents in text below.

### Polymerised Glycerine, "D" Glycerine, Diglycerine or Diglycerol

WHEN glycerol is heated in the presence of various alkaline salts—and even when heated alone at ordinary pressures—polymers are formed with the elimination of water, expressible by the general equation :—

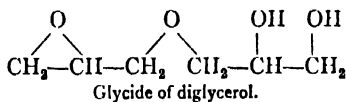
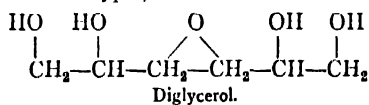


For example, if one molecule of water be extracted from two molecules of glycerol, diglycerol



results.

Rayner suggests that the conversion of glycerol to volatile polymerisation products gives rise to substances of at least two different types, thus :—



He supports this contention by isolating two different products which correspond closely in analysis to these formulæ, but the product of the diglycerol type had a viscosity thirteen times that of glycerol, while the other product of glycide type had a viscosity only five times that of glycerol.

The presence of nitrated diglycerol in nitroglycerol lowers the freezing point and thus obviates the danger of freezing.

Hence there have come on the market a number of "non-freezing" dynamites and blasting mixtures which can be used in cold weather.

**Manufacture of Diglycerol.**—*Claessen* (German Patent, 198,768, 1907) prepares polyglycerines by heating glycerol with 0.5 per cent. of alkali. By nitrating, an explosive resistant to freezing is obtained.

Polymers of glycerol ("condensed glycerols") are prepared on a commercial scale by heating the glycerol at ordinary pressure to 240° C. in a current of carbon dioxide<sup>1</sup> or other non-oxidising gas (which helps to remove the liberated water),

<sup>1</sup> *Nobel's Explosive Co., Rintoul, and Innes*, English Patent, 24,668, 1910.

## THE MODERN SOAP AND DETERGENT INDUSTRY

with or without the addition of substances to accelerate the polymerisation. Also by heating the glycerol with small amounts of caustic soda or sodium acetate,<sup>1</sup> or calcium hydroxide or bromine.

By using as an accelerator 0.5 per cent. of sodium carbonate it is claimed that the final product contains 40 per cent. of diglycerol.

It is stated<sup>2</sup> that ordinary commercial polymerised glycerol is manufactured by adding 0.2 per cent. sodium bicarbonate to glycerol of the dynamite grade and heating at 260° C. under a slight vacuum (to draw off evolved water) for several hours until the correct percentage of polymers are contained.

Hiffert (U.S. Patent, 126,467, 1912) claims that diglycerol may be prepared in a tolerably pure state by using 0.05 per cent. of iodine as a catalyst. An excessive amount of iodine results in rapid polymerisation, but also converts about 10 per cent. of the glycerol into aldehydes.

**Properties of Diglycerol.**—*Lewis (loc. cit.)* prepared his diglycerol by adding 0.05 per cent. of iodine to glycerol and heating at 210° C. for two hours with continual agitation. On distillation under reduced pressure, an 85 per cent. yield was obtained of a water-white viscous and very hygroscopic fluid, boiling freely at 257°–260° C. at 30 mm. pressure. The diglycerol obtained was soluble in water and insoluble in ether. The specific gravity at 20°/20° C. was 1.3215; 30°/30° C., 1.3183; 40°/40° C., 1.3140. The specific gravity is thus higher than that of pure glycerol. It contained C 43.10 per cent., H 8.59 per cent. (C<sub>8</sub>H<sub>14</sub>O<sub>3</sub> requires C 43.35, H 8.50 per cent.). The boiling point of this product agrees with that of the diglycerol (bisdioxypyrrol oxide) obtained by Nef, which is given as 261°–262° C. at 27 mm. ("Annalen," 335, 239.)

**Estimation of the Amount of Polymerised Glycerol in a Sample of Glycerol.**—The quantity of polymerised glycerol in a sample of glycerol may be estimated either by taking the specific gravity of the sample or by determining its actin value.

**Specific Gravity Method.**—A series of mixtures of pure glycerol and pure diglycerol are made, and the various specific gravities are plotted on a curve AB (Fig. 1).

When the percentage of diglycerol is 0 (only pure glycerol being present), the specific gravity is OA; but when the percentage of diglycerol is 100 (no glycerol being present), the specific gravity of the mixture is EB.

Hence if the specific gravity indicated by a given mixture is PC, the corresponding percentage of diglycerol present is indicated by OP.

Since

$$\frac{CM}{BN} = \frac{AM}{AN} = \frac{OP}{OE}$$

then if

$$\begin{aligned} y_1 &= OA = \text{specific gravity of pure glycerol,} \\ y_2 &= BE = \text{specific gravity of pure diglycerol,} \\ y &= CP = \text{specific gravity of the mixture,} \\ x &= OP = \text{required percentage of diglycerol in mixture,} \\ OE &= 100. \end{aligned}$$

Then

$$\frac{y - y_1}{y_2 - y_1} = \frac{x}{100}$$

or

$$x = 100 \times \frac{y - y_1}{y_2 - y_1}$$

The following table<sup>3</sup> has been drawn up on this basis, the specific gravities of the mixtures having been determined at 26.45°/26.45° C. on account of the high viscosity of the polymerised glycerol and the difficulty of eliminating air bubbles at lower temperatures :—

<sup>1</sup> *Fleming*, U.S. Patent, 978,443, 969,159; English Patent, 15,829, 1910.

<sup>2</sup> *Lawrie*, Allan's "Commercial Organic Analysis," 1924, vol. ii., p. 725.

<sup>3</sup> *Lawrie*, Allan's "Commercial Analysis," 1924, vol. ii., p. 726.

# ESTIMATION OF POLYMERISED GLYCEROL

Specific Gravity.	Specific Gravity, "D" Glycerine, Percentage; Polymers, Specific Gravity at 26.45°/26.45° C.										Average Difference.
	0	1	2	3	4	5	6	7	8	9	
1.259	5.25	5.75	6.50	7.00	7.50	8.00	8.50	9.00	9.75	10.25	0.500
1.260	10.75	11.25	11.75	12.50	13.00	13.50	14.00	14.50	15.00	15.75	0.500
1.261	16.25	16.75	17.25	17.75	18.25	18.75	19.25	20.00	20.50	21.00	0.475
1.262	21.50	22.25	22.75	23.25	23.75	24.25	24.75	25.25	26.00	26.50	0.500
1.263	27.00	27.50	28.00	28.50	29.25	29.75	30.25	30.75	31.25	31.75	0.475
1.264	32.50	33.00	33.50	34.00	34.50	35.00	35.50	36.25	36.75	37.25	0.475
1.265	37.75	38.25	38.75	39.50	40.00	40.50	41.00	41.50	42.00	42.50	0.475
1.266	43.00	43.75	44.25	44.75	45.25	45.75	46.50	47.00	47.50	48.00	0.500
1.267	48.50	49.25	49.75	50.25	50.75	51.25	51.75	52.25	52.75	53.25	0.475
1.268	53.75	54.50	55.00	55.50	56.00	56.50	57.00	57.50	58.00	58.50	0.475
1.269	59.00	59.75	60.25	60.75	61.25	61.75	62.25	62.75	63.25	63.75	0.475
Average difference	4.89	4.90	4.89	4.89	4.89	4.89	4.89	4.89	4.86	4.86	0.484

## Estimation of Polyglycerols by Specific Gravity Method

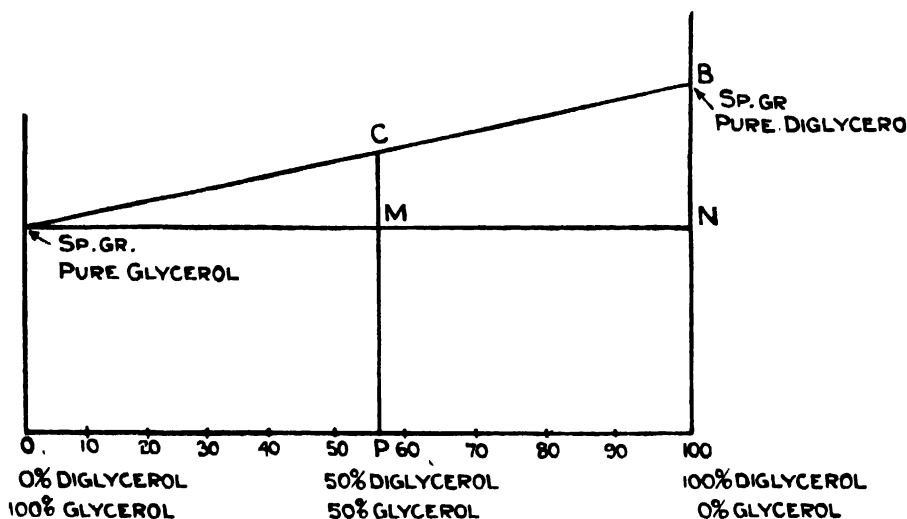


FIG. 1.

**Acetin Method of Estimating the Amount of Diglycerol Present in Glycerol.**—Here also a series of estimations are made of the *acetin* values (see below analyses of glycerol) of the pure glycerol and the pure diglycerol and of mixtures of the two, and a curve is constructed as before, from which the quantity of polymer can be read off which corresponds to any given acetin value of the mixture. Of course, instead of taking 100 per cent. glycerol as the starting point, weaker solutions may be taken.

This method, however, involving as it does chemical analysis, is not usually adopted on plant operations.

Estimation of Polyglycerols by Acetin Method

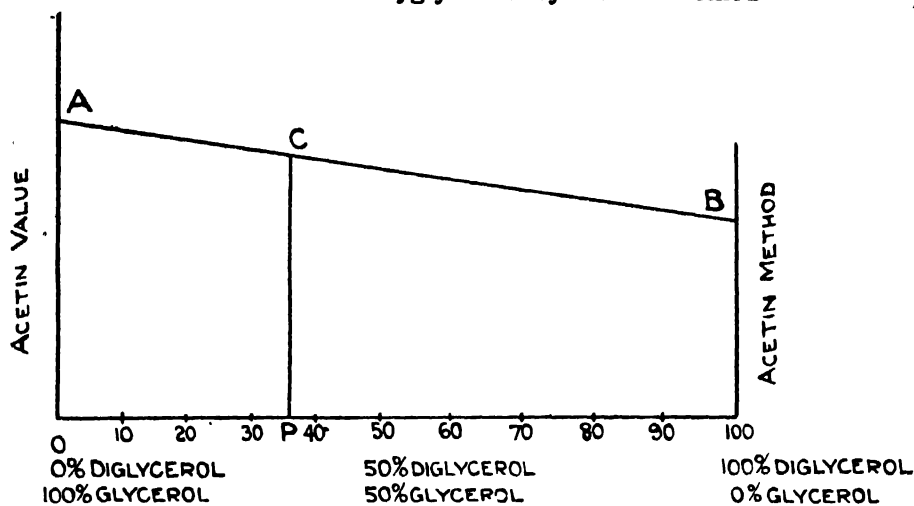


FIG. 2.

## CHAPTER II

# GLYCEROL SUBSTITUTES

DURING the Great War the shortage of fats in Germany and the large demand of glycerol for explosives led to the vigorous search for efficient substitutes.

The following patents deal with the subject :—

**Glycerine Substitute** (Ester Salts of Phthalic Acid) (*O. Rossler*, Dresden, German Patent, 313,059, 23rd August 1917).—Ester salts of phthalic acid soluble in water are used as glycerine substitutes. One carboxyl group of the phthalic acid is esterified with a monohydric alcohol and the other group is combined with a metallic base, such as sodium, to form a salt soluble in water. The ester salts are used in moderately dilute solution.

**Glycerine Substitute** (from Lactates) (*Chem. Fabr. vorm. Goldenberg Germont und Co.*, German Patent, 303,991, 8th February 1916).—Aqueous solutions of alkali lactates may be used in place of glycerol for many purposes, *e.g.*, lubrication of machinery, softening of leather, etc. An 80 per cent. solution of sodium lactate boils at 126° C. and loses no water by evaporation at the ordinary temperature; a 50 per cent. solution does not freeze at 60° C.

In German Patent, 332,167, they suggest mixing the alkali lactates with lactates of calcium, zinc, and magnesium.

**Glycerol Substitutes** (Per- and Perka-Glycerol): Alkali Lactates as (*C. Neuberg* and *E. Reinfurth*, *Ber.*, 1920, **53**, 1783-1791).—The technical uses of glycerol, apart from the production of explosives, depend on its viscosity, hygroscopicity, and neutrality; these properties are also exhibited by aqueous solutions of sodium and potassium lactates (per- and perka-glycerol respectively), which have been extensively used by the belligerent forces of the General Powers and for medical and cosmetic purposes during the late war. Economically their preparation permits a much better utilisation of the initial material (sugar, etc.), since this can be fermented so as to yield 95 per cent. and more lactic acid, whilst on the technical scale it only gives one-fifth to a quarter of its weight of glycerol; further, for many purposes the glycerol substitutes can be used in considerably more dilute solution than glycerol itself. The paper contains an extended series of tables and graphs showing the relationship between specific gravity and concentration of aqueous solutions of per- and perka-glycerol at 15° C., the freezing point of solutions of per-glycerol at different concentrations, the comparative freezing point of equimolar solutions of per-glycerol and glycerol, the boiling points of per-glycerol, the comparative hygroscopicity of solutions of glycerol and per-glycerol at 25° C., and the viscosity of per-glycerol.

According to *P. Panwitz* and *A. Beythien* (*Z. Unters. Nahr. Genussm.*, 1918, **35**, 385-387), a glycerol substitute sold under the name "perka-glycerol" consists of an aqueous solution containing 65-68 per cent. of potassium lactate.

**Glycerine Substitute for Technical, Pharmaceutical, and Cosmetic Purposes** (*Chem. Fabr. Florsheim, Dr H. Noerdlinger, Florsheim*, German Patent, 311,374, 3rd September 1916).—A substitute for glycerine is composed of magnesium butyrate, either alone or mixed with a small percentage of glycerine, alcohol, or other glycerine substitutes, magnesium chloride in particular.

**Glycerine for Medicinal Purposes: Substitute for** (*J. Lennox, Pharm. Jour.*, 1917, 98, 186).—Irish moss ( $\frac{1}{2}$  oz.) is boiled with water for fifteen minutes; the extract is made up to 19 fl. oz., and 1 oz. of glucose is added.

**Lubricating Oil and Glycerine (Dicresyl Carbonate as): Substitute for** (*Chem. Fabr. von Heyden A.-G.*, German Patent, 302,361, 27th February 1917).—Dicresyl carbonate is recommended as being cheaper than the tricresyl phosphate described in German Patent, 288,448, as a substitute for lubricating oil and glycerine.

*H. Wallasch* (German Patent, 325,647, 1919) makes a glycerine substitute by allowing formaldehyde and dicyanodiamide to react in the absence of a condensation agent.

The *Akt.-Ges. f. Anilinfabr.* (German Patent, 328,530, 1918) make a very viscous mixture from 180 parts of calcium chloride, 350 parts of water, and 465 parts of *betaine*. The mixture has specific gravity of 1.2485, which is equal to 94.5 per cent. glycerol.

*L. Cassella & Co.* (German Patent, 343,148, 1918) make sweet viscid solutions for use as a substitute for glycerol by adding a small proportion of water to the compounds, either alone or in admixture, prepared by neutralising di-pyridine-betaine hydrochloride with sodium carbonate, calcium carbonate, or adding potassium iodide, mercuric chloride, or sodium salicylate.

**Ethylene Glycol** ( $\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$ ) is now used extensively as a substitute for glycerol. The use extends both to the manufacture of dynamite and as a "*radiator compound*" to stop freezing in motor car radiators. Colourless viscid liquid, B.P.  $197^\circ \text{C}$ .; density, 1.125 ( $0^\circ$ ). Miscible with water. Oxidised by  $\text{HNO}_3$  yields oxalic acid. Heated with  $\text{KHSO}_4$  yields acetaldehyde. Acetate, B.P.  $186^\circ$ . Benzoate, M.P.  $73^\circ$ .

## SECTION VI

# Commercial Valuation and Analyses of Glycerol





# CHAPTER I

## GENERAL SUMMARY OF METHODS OF DETECTING AND ESTIMATING GLYCEROL

### LITERATURE

- ALLAN'S "Commercial Organic Analysis," vol. ii., 5th Edition. Article by Dr J. W. Lawrie gives an excellent and exhaustive account of the whole subject.
- LEWKOWITSCH. "Chemical Technology and Analysis of Oils, Fats, and Waxes," vol. iii.
- W. H. SIMMONS and H. A. APPLETON. "The Handbook of Soap Manufacture" (1908), pp. 136, 137, gives a clear summary of methods applicable to soapworks.
- "The Analysis of Crude Glycerine," International Standards Methods, 1911.
- "Ardeer Factory Analytical Method Book," Part II. A, Method No. 33, *Jour. Ind. Eng. Chem.*, 1910, 2, 11; 1911, 3, 679.
- Also literature quoted in text.

THE analytical determination of glycerol has become of considerable importance, since the latter substance has become of very considerable value in the arts within recent years.

In the following chapter we give a survey of the general methods adopted, fuller details being given in the later chapters where necessary, and also the original authorities should be referred to when necessary.

**Detection of Glycerol.**—(1) To detect glycerol, dry the substance thoroughly at 100° C., mix with twice its weight of finely powdered potassium hydrogen sulphate, and heat (on the sand bath) in a small flask fitted with a leading tube passing into a test tube placed in a freezing mixture. In the presence of glycerol the characteristically smelling acrolein will be evolved, the presence of which may be confirmed by adding to the liquid in the test tube a few drops of a mixture of 3 g. of silver nitrate in 30 g. ammonia (sp. gr. 0.923) and 3 g. of sodium hydroxide in 30 g. water. A silver mirror should rapidly appear.

(2) Boil the solution to be tested with a very small amount of pyrogallol and a few drops of sulphuric acid.

A red colour, changing to violet-red on adding stannic chloride, is given by glycerol and also by other substances.

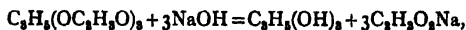
(3) Place the mass to be tested in a still, heat to 250° C., and distil in a current of steam superheated to 250° C. Any glycerol present distils over and may be collected and tested for.

**Estimation of Glycerol.**—The following methods are well known :—

(1) **Acetin Method.**—A weighed portion of this glycerol is acetylated, as described below with acetic anhydride and dried sodium acetate, the excess of acetic acid *exactly* neutralised with NaOH in the cold, and the number of acetyl

## 4 THE MODERN SOAP AND DETERGENT INDUSTRY

groups in the  $C_3H_5(OC_2H_5O)_3$  determined by adding *excess* of standard NaOH, and boiling and titrating back with acid. From the equation—



it will be seen that 3 molecules of NaOH used up denote 1 molecule of glycerol present. The amount of glycerol in the whole may then be estimated.

The method was invented by *Benedikt* and *Cantor* (*Jour. Soc. Chem. Ind.*, 1888, 7, 696), and is the one recommended for accurate work by the International Standard Committee.

Full details of carrying out the estimation are given in Chapter II. below, together with critical remarks on it.

(2) **The Bichromate Method.**—This method was originally invented by O. Hehner (see *Jour. Soc. Chem. Ind.*, 1889, 4-9), but the modification introduced by Richardson and Jaffe (*ibid.*, 1898, 17, 330; 1899, 331; see also *Banninger, Zeits. f. Angew. Chem.*, 1907, 1993) is somewhat more rapid and will be described here :—

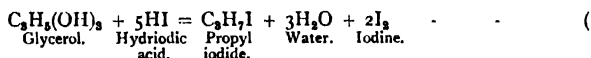
When glycerol is heated with potassium dichromate solution and concentrated sulphuric acid, the glycerol is completely oxidised to carbon dioxide and water, thus :—



Consequently for every 1 g. of glycerol oxidised 7.486 g. of dichromate disappear. Consequently if we take a solution of the latter containing 74.86 g. of dichromate per litre it will be seen that 1 c.c. of the dichromate solution will oxidise 0.01 g. of glycerol.

Exact details of carrying out this method is given below in Chapter II.

(3) **Zeisel and Fanto's Method.**—When glycerol is boiled in a flask fitted with a reflux condenser with excess of concentrated hydriodic acid (sp. gr. 1.7; b.p. 127° C.), it is changed quantitatively into isopropyl iodide, thus :—



The reflux condenser is filled with water at 60° C. The propyl iodide distils over and bubbles through a Geisler tube containing red phosphorus and water, immersed in water at 60°-70° C. Any hydriodic acid vapours is retained here. The propyl iodide vapours pass on and bubble through a solution of alcoholic *silver nitrate*.

The propyl iodide is decomposed, thus :—



The silver iodide is collected and weighed. Then  $C_3H_5(OH)_3$  corresponds to AgI, or 92 g. glycerol correspond to 234.8 g. AgI, or 1 g. AgI represents 0.3918 g. of glycerol.

Exact details of carrying out the method will be found in Allan's "Commercial Analysis," vol. ii., 5th Edition, 1924, p. 668, to which the reader is referred.

See also *Zeisel and Fanto, Zeit. landw. Versuchswesen Oest.*, 1902, 5, 729. The method, however, is hardly suitable for a works laboratory on account of the skill required.

(4) **Oxidation by Potassium Permanganate.**—Glycerol may be estimated by oxidising with potassium permanganate solution, whereby it is oxidised to oxalic acid, which is precipitated with calcium chloride and the resulting calcium oxalate titrated with N/10 permanganate. 1 c.c. N/10 permanganate = 0.0045 g. oxalic acid.  $H_2C_2O_4 = 0.0046$  g. glycerol.

The dichromate and acetic method has completely displaced this method. See, however, *Benedikt and Zsigmondy, Chem. Zeit.*, 1885, 9, 975. *Mangold* (*Jour. Soc. Chem. Ind.*, 1891, 10, 803). Full details are given in *Allan's "Commercial Analysis,"* 5th Edition, 1924, vol. ii., p. 660, to which the reader is referred.

(5) **Acetone Extraction Method.**—The glycerol solution is evaporated, mixed with sand or dehydrated sodium sulphate, and the mass extracted with acetone.

The glycerol passes into solution and is estimated by evaporation and weighing.

The method is lacking in accuracy but is useful for estimating the glycerol in fermenting beverages (see below).

### Remarks on the Acetin and Bichromate

**Methods.**—The acetin and bichromate methods have established themselves in practice, and under certain conditions each one will yield reliable results.

The disadvantage of the bichromate method is that all **oxidisable** matter present, in addition to the glycerol, is calculated as glycerol so that the results tend to be too high. For example, soaps are sometimes bleached by means of hydrosulphite, and a trace of this chemical would at once reduce the bichromate and increase the apparent amount of glycerol; also any polyglycerols present would be returned as glycerol.

According to *F. Schulze* (*Chem. Zeit.*, 1905, **29**, 979), the bichromate method gives results about 10 per cent. too high, and is valid only in the absence of phosphoric acid.

On the other hand, the acetin method tends to yield too low results.

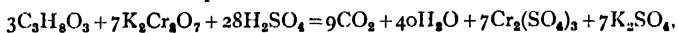
*Lewkowitsch* (see "Technology of Oils, Fats, and Waxes") has shown that the method gives closely concordant results in the case of moderately pure "**crude glycerol**," and recommends its adoption in all cases in which the glycerol is first isolated in a fairly pure state, especially in the case of **soap crude glycerol**, because polyglycerols (contained in residues from the glycerol stills, see above, p. 34, Section II.), if admixed with crude glycerol, would be oxidised by the bichromate, and thus calculated to glycerol; whereas the polyglycerols are not converted into esters on boiling with acetic anhydride; whereas for ascertaining the proportion of glycerol in its pure dilute aqueous solution the dichromate method is best, although it gives too high results with impure glycerine.

For soap works laboratory it usually suffices to determine the glycerol by one process only, in the ordinary course, the other process being used as a check in case of doubt or dispute. The acetin process is usually recommended.

**Estimation of Glycerol in Fats.**—The glycerol is separated from the fat by saponifying with alcoholic KOH, filtering the soap solution, setting free the fatty acids by  $\text{H}_2\text{SO}_4$ , and filtering them off. The aqueous extract, containing all the glycerol, is neutralised with  $\text{BaCO}_3$ , evaporated, and the glycerol extracted with ether. On evaporating the ether the crude glycerol is left and may be weighed.

The actual amount of glycerol in this crude glycerol may now be determined by the **acetin** or the **dichromate process**, as described in the next chapter.

**Estimation of Glycerol in Soap Lyes.**—250 c.c. of soap lye are acidified with  $\text{H}_2\text{SO}_4$ , the fatty acids filtered off, lead acetate added, the precipitate filtered off, the solution evaporated, made up to 100 c.c., and 25 c.c. are boiled thirty minutes with 25 c.c. concentrated  $\text{H}_2\text{SO}_4$  and 40 c.c.  $\text{K}_2\text{C}_2\text{O}_7$  solution containing 75 g. per litre. From the equation—



it will be seen that for every 1 g. of glycerol oxidised 7.5 g. of dichromate disappear, *i.e.*, 100 c.c. of dichromate solution are used up. The exact strength of dichromate before and after boiling is found by titrating with ferrous ammonium sulphate in the ordinary way. From the loss in strength of the dichromate the amount of glycerol can be calculated. The results are usually too high.

*Lewkowitsch* ("Technology of Oils, Fats, and Waxes") suggests the following procedure if sulphur compounds are absent: 1,000 g. are heated to boiling, acidified with hydrochloric acid, filtered from the oily layer of fatty acids which separate, neutralised, treated with lead acetate, filtered from the precipitate, and the clear solution boiled down, the separated salt scooped out and sucked dry on the filter pump. When finally only a few cubic centimetres of liquid are left,

## 6 THE MODERN SOAP AND DETERGENT INDUSTRY

these are added to the salt and the latter thoroughly extracted with a mixture of 3 parts of methylated spirit and 1 of ether. The ethereal extract is evaporated on the water bath and the crude glycerol thus obtained estimated by the acetin process described above.

*Lewkowitsch* suggests obtaining approximate results rapidly by heating the alcohol-ether residue to 150° C., weighing, burning off the glycerol, and weighing again. The difference gives the approximate weight of pure glycerol.

**Loss of Glycerol by Evaporation.**—*O. Hehner* (*Analyst*, 1887, 12, 65) has shown that glycerol is not volatilised with aqueous vapour from dilute solution. When a solution is evaporated at 100° C., appreciable loss does not occur until the solution contains about 70 per cent.

After this stage an appreciable loss will occur, as was shown by *Nessler and Barth* (*Zeit. Anal. Chem.*, 1884, 23, 323), who showed, for example, that 1 g. of glycerol exposed in a platinum dish to 100° C. on a boiling water bath lost 46 mg. in the first two hours, 29 mg. in the second two hours, and 21 mg. in the third three hours.

Hence any process of estimating glycerol which involves the evaporation of an aqueous or alcoholic solution of glycerol must be deficient in quantitative accuracy.

**Estimation of Glycerol in Dry Wines** (see "Off. and Tent. Methods of Anal. of the Assoc. Agr. Chem.," 1919, 1920, p. 174).

(1) **By Direct Weighing.**—Evaporate 100 c.c. to about 10 c.c. on the water bath, add 5 g. of fine sand and 4.5 c.c. of milk of lime for each gram of extract present. Evaporate nearly to dryness, triturate with 50 c.c. absolute alcohol, heat to boiling, filter, and wash several times with 10 c.c. of alcohol until the washings amount to 150 c.c. This extracts all the glycerol. Evaporate filtrate to a syrup, transfer to a small stoppered bottle by washing with 20 c.c. of absolute alcohol, and add 30 c.c. of absolute ether (best in three portions), shaking well after each addition.

Any sugars or gums present are insoluble in the mixture of alcohol and ether, whereas the glycerol dissolves.

Filter from insoluble gum, etc., evaporate on W.R., dry at 100° C. for one hour, weigh, ignite, and weigh again.

The loss of weight equals weight of glycerol in 100 c.c. wine.

(2) **Dichromate Method.**—Proceed as before, repeatedly filtering or centrifuging from the precipitated gums and proteins. Finally, treat residue with silver carbonate and basic lead acid solution; filter and then oxidise the residue with concentrated potassium dichromate solution and sulphuric acid. Titrate loss of dichromate with ferrous ammonium sulphate in the ordinary way.

Full details of carrying out the estimation are given in *Allan's "Commercial Analysis,"* 5th Edition, 1924, vol. ii., p. 736, to which the reader is referred. See also *Bey, Compt. Rend.*, 1910, 151, 80; *Bull. Soc. Chem.*, 1912, 11, 618.

**Estimation of Glycerol in Crude Fermentation Glycerol.**—Fermentation glycerol (see p. 3, Section III.) became an important new source during the war, and consequently the estimation of glycerol in fermenting liquids became a matter of some importance.

Numerous methods were published, and a full account of these methods may be found in *Allan's "Commercial Analysis,"* 5th edition, 1924, vol. ii., p. 728 *et seq.*, to which the reader is referred for more exact details. The following methods are usual:—

(1) **Acetone Extraction Method.**—The fermenting liquid is evaporated to a syrup, mixed to a paste with sand, dried at 80° C. on the water bath, extracted

in a Soxhlet apparatus with chemically pure dry acetone, which dissolves the glycerol but leaves behind the gums and salts.

The acetone is evaporated and the residue consists of glycerol. The percentage of pure glycerol in this is then ascertained by the **acetin** method. See also *Shukoff* and *Schestakoff*, *Zeit. Angew. Chem.*, 1905, **18**, 294. For a more exact method see *Fachini* and *Fortor*, *Ind. Chem.*, **10**, 3111-3114.

(2) **Distillation Method.**—The fermented liquid is evaporated to a syrup, introduced into a flask or still, which is then heated in a bath to  $170^{\circ}\text{C}$ ., while a current of superheated steam at  $170^{\circ}\text{C}$ . is passed through the liquid, while a slight vacuum is maintained.

The glycerol present distils over, is condensed, evaporated, and its glycerol content estimated either by taking a specific gravity or by the acetin method.

For further details see *Allan's "Commercial Analysis,"* 5th Edition, 1924, vol. ii., p. 732 *et seq.* See also *K. Fleischer*, *Zeit. Anal. Chem.*, 1921, **60**, 330.

## CHAPTER II

# UNDISTILLED GLYCEROL—INTERNATIONAL STANDARDS METHODS (I.S.M.) OF 1911 FOR THE ANALYSIS OF CRUDE GLY- CERINE

### ANALYSIS OF CRUDE GLYCERINE

#### REPORT

#### International Standards Methods, 1911

THE valuation of crude glycerine has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods and processes of analyses, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerine analysis; so, with this object in view, Committees were formed in America, France, Germany, and Great Britain. These Committees worked, in the first instance, independently, but were ultimately brought together, and after a series of Conferences the conclusions arrived at by the various Committees were summarised and drawn up in the form in which they are now presented. The methods detailed in this Report have the unanimous support of each of the above Committees, and are strongly recommended by them as International Standards.

Producers, consumers, and analysts were represented on the Committees. It is hoped that the conclusions arrived at will be found acceptable by all parties interested.

### CONSTITUTION OF COMMITTEES

#### American Committee

A. M. Comey, of Messrs E. I. du Pont de Nemours Powder Co.  
R. E. Devine, Glycerine Specialist, Detroit, Michigan.  
S. S. Emery, of Messrs du Pont Powder Co., Colorado Plant.  
A. C. Langmuir, of Messrs Marx & Rawolle, New York.  
J. W. Loveland, of Messrs B. T. Babbit's Soap Works, New York.  
W. H. Low, of Messrs The Cudahy Packing Co., So. Omaha.

#### British Committees

##### Executive Committee

T. A. Cook, of Messrs E. Cook & Co. Ltd., London.  
W. W. Gossage, of Messrs W. Gossage & Sons, Widnes.  
J. Gray, of Messrs Lever Brothers Ltd., Port Sunlight.  
J. Griffiths or E. Tappley, of Messrs Price's Patent Candle Co. Ltd.  
C. Haslam, of Messrs J. Crosfield & Sons Ltd., Warrington.  
J. M'Callum, of Messrs Isdale & M'Callum, Paisley.

**Expert Committee****Appointed by British Executive Committee**

J. Allan, of Messrs J. Crosfield & Sons Ltd., Warrington  
 J. L. Buchanan, of Messrs Lever Brothers Ltd., Port Sunlight.  
 O. Hehner, Analyst, London.  
 J. B. M'Arthur, of Messrs Price's Patent Candle Co. Ltd.  
 W. H. Phillips, of Messrs E. Cook & Co. Ltd., London.  
 P. Tainsh, of Messrs Nobel's Explosive Co. Ltd., Stevenston.  
 F. Tate, of Messrs A. Norman Tate & Co., Analysts, Liverpool.

**French Representative**

M. Vizern, of Messrs Vizern & Guillot, Marseilles.

**German Committee**

A. C. Geitel, of Messrs The Royal Stearin Candle Works, Gouda, in Gouda.  
 W. Grunewald, of Messrs C. F. Boehringer & Soehne, Mannheim-Waldhof.  
 P. Guckel, of Messrs The Dynamit Aktien Gesellschaft, Hamburg.  
 A. Jacobi, of Messrs A. Jacobi, Darmstadt.  
 V. Knapp, of Messrs G. H. Orth, Barmen.

**METHODS OF CRUDE GLYCERINE ANALYSIS****RECOMMENDED BY THE INTERNATIONAL COMMITTEES****Sampling**

The most satisfactory method available for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (Appendix I.), then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled. Glycerine which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken, including any deposit.

The usual method of sampling crude glycerine hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerine contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates viscous glycerines run into the tube very slowly, so, owing to the time occupied, it is impossible to take a complete section of the sample. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the

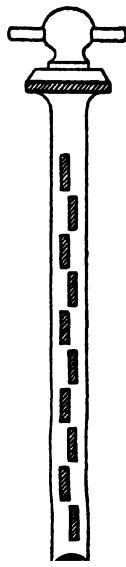


FIG. 1.

Glycerol Sampler.  
 SEC. VI.

drum. By this arrangement the glycerine fills into the sampler almost instantaneously. There is also a number of ports cut at the bottom of the sampler which render it possible to take a sample without turning the drum. The instrument is so constructed that all the

of larger section (1 in.) it is possible to arrange a third motion whereby the bottom ports only are open for emptying, but in samplers of smaller dimensions ( $\frac{3}{4}$  in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains suspended salt the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum; it is therefore recommended that the drum should be sampled before the salt has settled.

A sampler 1 in. dia. withdraws approximately 10 oz. from a 10-cwt. drum.  
 "  $\frac{3}{4}$  in. dia. " " 5 oz. " 10-cwt. "

### Analysis

(1) **Determination of Free Caustic Alkali.**—Weigh 20 g. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution make up to the mark, and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid (N/1). Calculate to percentage of  $\text{Na}_2\text{O}$  existing as caustic alkali.

(2) **Determination of Ash and Total Alkalinity.**—Weigh 2.5 g. of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

(3) **Determination of Alkali Present as Carbonate.**—Take 10 g. of the sample, dilute with 50 c.c. distilled water, add sufficient N/1 acid to neutralise the total alkali found at (2), boil under a reflux condenser for fifteen to twenty minutes, wash down the condenser tube with distilled water free from carbon dioxide, and titrate back with N/1 NaOH, using phenolphthalein as indicator. Calculate the percentage of  $\text{Na}_2\text{O}$ . Deduct the  $\text{Na}_2\text{O}$  found in (1). The difference is the percentage of  $\text{Na}_2\text{O}$  existing as carbonate.

(4) **Alkali Combined with Organic Acids.**—The sum of the percentages  $\text{Na}_2\text{O}$  found at (1) and (3) deducted from the percentage found at (2) is a measure of the  $\text{Na}_2\text{O}$  or other alkali combined with organic acids.

(5) **Determination of Acidity.**—Take 10 g. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with N/1 NaOH and phenolphthalein. Express in terms of  $\text{Na}_2\text{O}$  required to neutralise 100 g.

(6) **Determination of Total Residue at 160° C.**—For this determination the crude glycerine should be slightly alkaline with  $\text{Na}_2\text{CO}_3$  not exceeding equivalent of 0.2 per cent.  $\text{Na}_2\text{O}$ , in order to prevent loss of organic acids. To avoid formation of polyglycerols this alkalinity must not be exceeded.



## UNDISTILLED GLYCEROL

**Preparation of Glycerine.**—10 g. of the sample are weighed into a 100 c.c. flask diluted with water, and the calculated quantity of  $N/1$   $HCl$  or  $Na_2CO_3$  added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed petrie or similar dish 2.5 in. diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30-40 mg.

**Evaporation of the Glycerine.**—The dish is placed on a water bath (the top of the  $160^\circ$  oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate  $\frac{3}{4}$  in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to  $160^\circ C.$  with the door closed, a temperature of  $130^\circ$ - $140^\circ$  can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

An addition of 0.5-1 c.c. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at  $160^\circ C.$  it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours is required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at  $160^\circ C.$  for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid, and weighed. The treatment with water, etc., is repeated until a constant loss of 1-1.5 mg. per hour is obtained.

**Corrections to be Applied to the Weight of the Total Residue.**—In the case of acid glycerine a correction must be made for the alkali added. 1 c.c.  $N/1$  alkali represents an addition of 0.022 g. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the  $NaOH$  and  $Na_2CO_3$  to  $NaCl$ . The corrected weight, multiplied by 100, gives the percentage of total residue at  $160^\circ C.$

Preserve the total residue for the determination of the non-volatile acetylisable impurities.

(7) **Organic Residue.**—Subtract the ash from the total residue at  $160^\circ C.$  Report as organic residue at  $160^\circ C.$  (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition and that the  $CO_3$  radical thus derived is not included in the organic residue.)

(8) **Moisture.**—This test is based on the fact that glycerine can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride. 2-3 g. of very pure bulky asbestos freed from acid-soluble material, which has been previously dried in a water oven, are placed in a small stoppered weighing bottle of about 15 c.c. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1-2 mm. of mercury, until constant in weight. From 1-1.5 g. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken and the bottle replaced in the desiccator under 1-2 mm. pressure until constant in weight.

At 15° C. the weight is constant in about forty-eight hours. At lower temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

### ACETIN PROCESS FOR GLYCEROL DETERMINATION

This process is the one agreed upon at a Conference of Delegates from the American, British, French, and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerines the results are identical with those of the bichromate process. For the application of this process the crude glycerine should not contain over 50 per cent. water.

#### Reagents Required

(A) **Best Acetic Anhydride.**—This should be carefully selected. A good sample must not require more than 0.1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7.5 c.c. Only a slight colour should develop during digestion of the blank.

(B) **Pure Fused Sodium Acetate.**—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

(C) **A Solution of Caustic Soda for Neutralising, of about N/1 Strength, Free from Carbonate.**—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) **N/1 Caustic Soda, Free from Carbonate.**—Prepared as above and carefully standardised.

Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) **N/1 Acid.**—Carefully standardised.

(F) **Phenolphthalein Solution.**—0.5 per cent. phenolphthalein in alcohol, and neutralise.

#### The Method

Into a narrow mouthed flask (preferably round bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25-1.5 g. of the glycerine. Add first about 3 g. of the anhydrous sodium acetate, then 7.5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon dioxide-free distilled water heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid

any sudden rush of vapours from the flask on adding the water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed,  $80^{\circ}\text{C}$ . until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (F), then run in a caustic soda solution (C) or (D) until a faint pinkish yellow colour appears throughout the solution. This neutralisation must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of  $\text{N}/1$  NaOH (D), and note carefully the exact amount. Boil gently for fifteen minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of NaOH with  $\text{N}/1$  acid (E) until the pinkish yellow or chosen end point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end point taken.

From the  $\text{N}/1$  NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below.

$$1 \text{ c.c. of } \text{N}/1 \text{ NaOH} = 0.03069 \text{ g. of glycerol.}$$

The coefficient of expansion for normal solutions is approximately 0.00033 per c.c. for each degree C. A correction should be made on this account if necessary.

**Blank Test.**—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid, it is not necessary to add more than 5 c.c. of the  $\text{N}/1$  alkali (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

#### Determination of the Glycerol Value of the Acetylisable Impurities.

—The total residue at  $160^{\circ}\text{C}$ . is dissolved in 1 or 2 c.c. of water, washed into a clean acetylisng flask 120 c.c. capacity, and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determination before described. Calculate the result to glycerol.

**Analysis of Acetic Anhydride.**—Into a weighed stoppered vessel, containing 10-20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper, and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenolphthalein, and titrate with  $\text{N}/1$  NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing bottle containing a known weight of recently

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distilled aniline (from 10-20 c.c.) measure about 2 c.c. of the sample; stopper, mix, allow to cool, and weigh. Wash contents into about 200 c.c. cold water, and titrate acidity as before. This yields the acidity due to the original, pre-formed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 g.) and double result, obtaining c.c. N/1 NaOH per 100-g. sample. 1 c.c. NaOH equals 0.0510 anhydride.

### BICHROMATE PROCESS FOR GLYCEROL DETERMINATION

#### Reagents Required

(A) **Pure Potassium Bichromate** powdered and dried in air free from dust or organic vapours, at 110°-120° C. This is taken as the standard.

(B) **Dilute Bichromate Solution.**—7.4564 g. of the above bichromate (A) are dissolved in distilled water and the solution made up to 1 litre at 15.5° C.

(C) **Ferrous Ammonium Sulphate.**—Dissolve 3.7282 g. of potassium bichromate (A) in 50 c.c. of water. Add 50 c.c. of 50 per cent. (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) **Silver Carbonate.**—This is prepared as required for each test from 140 c.c. of 0.5 per cent. silver sulphate solution by precipitation with about 4.9 c.c. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant, and wash once by decantation.

(E) **Subacetate of Lead.**—Boil a pure 10 per cent. solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) **Potassium Ferricyanide.**—A very dilute solution containing about 0.1 per cent.

#### The Method

Weigh 20 g. of the glycerine, dilute to 250 c.c., and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about ten minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (E); allow to stand a few minutes, dilute with distilled water to 100 c.c., and then add 0.15 c.c. to compensate for the volume of the precipitate; mix thoroughly, filter through an air-dry filter into a suitable narrow mouthed vessel, rejecting the first 10 c.c. and return filtrate if not clear and bright. Test a portion of the filtrate with little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c.c. is ample.) Occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerine should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previous

cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 g. of the powdered potassium bichromate (A). Rinse down the bichromate with 25 c.c. of water and stand with occasional shaking until all the bichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapours, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 g. glycerol equals 7.4564 g. bichromate.

1 g. bichromate equals 0.13411 g. glycerol.

### Notes

(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 c.c.

(4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

### Instructions for Calculating Actual Glycerol Content

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any be present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylisable impurities are present these are included in this figure.

### Notes and Recommendations

Experience has shown that in crude glycerine of good commercial quality the sum of water, total residue at 160° C., and corrected acetin result comes to within 0.5 of 100. Further, in such crudes the bichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol are present. Trimethylene glycol is more volatile than glycerine; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results of such distillates. Trimethylene glycol showing by the former method 80.69 per cent. and by the latter 138.3 per cent. expressed as glycerol.

In valuing crude glycerine for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates.

The methods for detecting and determining these impurities have not formed the subject of this investigation.

(Signed)

OTTO HEHNER, *Chairman.*

JOHN ALLAN.

JAMES B. M'ARTHUR.

W. H. PHILLIPS.

P. TAINSH.

FRANK TATE.

J. L. BUCHANAN, *Hon. Secretary.*

### Recommendations by Executive Committee

If the non-volatile organic residue at 160° C. in the case of a soap lye crude be over 2.5 per cent., *i.e.*, when not corrected for carbon dioxide in the ash, then the residue shall be examined by the acetin method, and any excess of glycerol found over 0.5 per cent. shall be deducted from the acetin figure.

In the case of saponification, distillation, and similar glycerines, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent. the organic residue must be acetylated, and any glycerol found (after making the deduction of 0.5 per cent.) shall be deducted from the percentage of glycerol found by the acetin test.

### Remarks on the International Methods by the American Committee.—

The following critical remarks on the preceding Report were made by the *American Sub-Committee on Glycerine Analysis*<sup>1</sup> :—

“A consideration of the methods turned in showed that the bichromate method was more commonly in use, but that there were apparently as many modifications as there were chemists using the process. The acetin method, although less frequently employed, was warmly recommended. It had suffered but little change from the original Benedikt and Cantor process.

“We have not discovered that the acetone extraction, permanganate oxidation, or determination as isopropyl iodide are anywhere in general use in the analysis of crudes.

“The bichromate method has in its various modifications travelled a long way from the original Hehner process, and most of the changes made have diminished rather than improved the accuracy of the method. The effectiveness of different purifying agents in removing organic impurities varies greatly, and yet there are in use : silver sulphate, copper sulphate, silver oxide, silver carbonate, silver acetate, and basic lead acetate, either alone or in combination with some silver salt. The basic lead acetate is seldom prepared in the same way and is of varying basicity. To completely oxidise glycerine with bichromate in presence of the lower fatty acids, which escape the purification, without at the same time partially oxidising the latter, is a problem requiring a nice adjustment of conditions. We find that widely varying proportions of sulphuric acid and bichromate are used and that the time of oxidation is not the same.

“As a result of our researches we have unanimously decided that the acetin method is the basis on which glycerine should be bought and sold. The bichromate method is of value in factory control and for routine work in the analysis of crudes of known good character. For this reason we have felt it necessary to retain the bichromate method in a properly standardised form, but we advise against its use in general analytical work.

<sup>1</sup> See “Report of the Sub-Committee on Glycerine Analyses,” by A. C. Langmuir, A. M. Comey, Robert E. Devine, S. S. Emery, J. W. Loveland, W. H. Low, *Jour. Ind. and Eng. Chem.*, 1911, 3, 679.

"Neither the acetin nor the bichromate method is correct in theory or practice on crudes containing trimethylenglycol or polyglycerols. We only know that the acetin is less affected by these substances than the bichromate. They are not precipitated by basic lead acetate or silver salts, and are therefore left to exert the full reducing power of the molecule on the bichromate. With the acetin, on the other hand, action is proportional to the number of OH groups directly attached to the chain. For example, a crude glycerine containing 80 per cent. glycerol and 1 per cent. trimethylenglycol will show by the bichromate method 81.38 per cent. and by the acetin method 80.81 per cent. glycerol. With triglycerol, a 1 per cent. addition would increase the bichromate test by 1.15 per cent. and the acetin by 0.64 per cent. A comparison of the results obtained by the acetin and bichromate methods will therefore often throw light on the nature and quantity of the impurities present.

"In the absence of a chemical method which will show glycerol only in such mixtures, we must therefore prefer the acetin method, because it gives the same results as the bichromate on pure glycerine and high-grade crudes and lower or much lower results on bad crudes. In the acetin method to be described the error caused by the presence of polyglycerols is partially offset by the determination of the acetylisable matter in the non-volatile residue at 160° C., which will hold the higher polyglycerols. The lower polyglycerols and trimethylenglycol are volatile at 160° C. and are therefore figured as glycerol. Trimethylenglycol is more volatile than glycerol and may be distilled off with the glycerine in the first portions of the distillate, where it may be determined by the spread between the acetin and bichromate tests.

"We have met with some bad crudes which cannot with safety be analysed by any chemical method known to us. The only method which will give even approximate results on crudes high in glycol or crudes containing still residues is a distillation in a still adapted to quantitative work. A crude containing a large amount of glycol tested 81.8 per cent. (bichromate), 76.2 per cent. (acetin), and 71.0 per cent. (by distillation). A crude made from still residues showed 73 per cent. by the bichromate method, 48 per cent. by the acetin method, and only 30 per cent. by distillation. These are extreme cases, but serve to show that a marked spread between the acetin and the bichromate tests is an indication that both are probably incorrect.

"The acetin is not looked upon with favour by some chemists on the ground that results are unreliable unless precautions are taken out of the reach of the busy laboratory. This opinion is largely the result of erroneous statements in the text-books and literature. The danger of saponifying triacetin by standing in aqueous solution and during neutralisation of the acetic acid is greatly exaggerated. A point in favour of acetin method is the avoidance of the purification required by the bichromate test.

"It is not possible to carry through as many acetin tests per day as bichromate, but with many crudes the difference between results is so wide that it is not any longer a question as to which method is the quicker or more convenient. The great increase in the price of crude glycerine, together with a falling off in quality, due to the use of impure fats and greases as well as the introduction of new methods of saponification, make it impossible to defend the bichromate method on the ground of convenience and custom. Valuable as this method has been in the past, it is unable to cope with many crudes of to-day."

**Later Work on the Determination of Glycerol in Commercial Glycerines and Soap Lyes.**—*M. Tortelli and A. Ceccherelli* (*Chem. Zeit.*, 1913, **37**, 1505-1506, 1573-1574; 1914, **38**, 3-5, 28-31, 46-48) carried out experiments upon the estimation of glycerol in commercial glycerines leading them to the conclusion that the acetin method prescribed in the International Standards Methods, 1911 (see above), gives low results, and they advocate the adoption of

the following modification of the Hehner bichromate process as being more accurate and more rapidly carried out. The following reagents are required :—

- (1) Pure potassium bichromate, small crystals.
- (2) Potassium bichromate solution, 74.564 g. per litre.
- (3) Dilute bichromate solution. Solution (2) diluted with water to ten times its volume.
- (4) Ferrous ammonium sulphate, chemically pure in small crystals; 2 g. titrated with solution (3) should require 33.5-33.6 c.c.
- (5) Ferrous ammonium sulphate solution; 200 g. are dissolved in water which has been made slightly acid with sulphuric acid and the solution made up to one litre; 10 c.c. should require 33.5-33.6 c.c. of the dilute bichromate solution.
- (6) Silver carbonate. Prepared as required by mixing 4.9 c.c. of N/1 sodium carbonate with 150 c.c. of 0.5 per cent. solution of silver sulphate. The precipitated silver carbonate is washed once by decantation and is then ready for use.
- (7) Basic lead acetate. A 10 per cent. solution of lead acetate is boiled with an excess of litharge for five hours, the volume being kept constant, and is then filtered hot.
- (8) Sodium sulphate solution, 10 per cent.
- (9) Potassium ferricyanide solution. A 0.1 per cent. solution which has been filtered through glass wool.
- (10) Sulphuric acid. The concentrated acid diluted with its own water.

**(A) Estimation of Glycerol in Crude Glycerine.**—(a) Preliminary test to determine approximately the glycerol content. About 5 g. of the sample are mixed with 10 c.c. of distilled water and 5 c.c. of basic lead acetate solution in a 100 c.c. glass-stoppered flask, the mixture being well shaken and allowed to stand for a few minutes. 10 c.c. of sodium sulphate solution are added, the volume of the solution made up to 100 c.c. with water and, after being well shaken and allowed to stand for a short time, the liquid is filtered through a dry filter paper. 10 c.c. of the filtrate are placed in a flask of 250-300 c.c. capacity, mixed with a few drops of dilute sulphuric acid, and then 50 c.c. of bichromate solution (reagent 2) and 50 c.c. of sulphuric acid (reagent 10) are added. The mixture is boiled gently for fifteen minutes over a direct flame and, after being cooled, the excess of bichromate is titrated with the ferrous iron solution.

(b) Final estimation of glycerol. A quantity of the sample which will be approximately equal to 5 g. of glycerol is diluted with water to 250 c.c. in a graduated flask. 25 c.c. of this solution are treated with the prescribed quantity of silver carbonate in a glass-stoppered 100 c.c. flask, and well shaken for five to ten minutes. Thereafter 5 c.c. of basic lead acetate are added, the mixture well shaken, and allowed to stand for two to three minutes. 5 c.c. of sodium sulphate solution are then added and, after shaking, the volume is made up to 100 c.c. and the liquid filtered through a dry filter; the first 10 c.c. being rejected, 25 c.c. of the filtrate are placed in the same flask as was used for the oxidation in the preliminary test, the liquid being made acid with 3 to 4 drops of sulphuric acid (1 : 5), and then 4 g. of potassium bichromate (reagent 1) and 25 c.c. of water are added. After the bichromate is dissolved, 50 c.c. of sulphuric acid (reagent 10) are added and the mixture gently boiled over a free flame for fifteen minutes. 4 g. of ferrous ammonium sulphate are added to the contents of the flask after these have cooled to room temperature and the excess of iron salt is titrated back with dilute bichromate solution (reagent 3). If the preliminary test has been properly carried out the titration should require about 25-30 c.c. of this solution.

**(B) Estimation of Glycerol in Soap Lyes.**—The amount of the sample taken is increased so as to give approximately corresponding amounts of glycerol in the test solution, and the lye is neutralised with acetic acid before adding the clarifying reagents. Extensive tables are given, the use of which avoids the tedious calculations which otherwise have to be made.



## CHAPTER III

# UNDISTILLED GLYCEROL—VALUATION OF CRUDE COMMERCIAL GLYCEROLS

### Valuation of Crude Commercial Glycerols

THE valuation of these glycerols depends upon the percentage of glycerol, specific gravity, organic impurity, and tests for the metals, arsenic, sulphur compounds, sugar, and fatty acids.

With **saponification glycerol** (see p. 3, Section I.) it is best to use the **acetin method** for determining the amount of glycerol present. The dichromate method gives high results (*vide* the *Analyst*, 1903, **28**, 104). The percentage of glycerol equals 85-90 per cent.

The **organic impurities** present are found by volatilising the glycerol by heating gradually several grains in a platinum dish to 160° C. During the heating the mass is best moistened with a few drops of moisture, so that the glycerol volatilises in steam. Too rapid heating yields non-volatile polyglycerols and too high results.

The product is dried to constant weight. The ash is obtained by ignition. The difference in weight gives the organic impurities.

**Crude Soap Lye Glycerol.**—The specific gravity should not be less than 1.3, and the percentage of glycerol should be at least 80 per cent. and is best determined by the **acetin** method. The **ash** may be as high as 10 per cent., and should consist mainly of salt. The following determinations should be made :—

**Organic impurities** are estimated in soap lye glycerol just as in saponification glycerol. **Protein matter** is always present, being derived from the envelopes of the fat globules and dissolved by the alkali. To estimate, precipitate with basic lead acetate and apply the Kjeldahl method. Percentage of  $N \times 6.25 =$  protein present in the precipitate.

**Fatty acids** may be detected by the turbidity they produce on acidifying the diluted glycerol. Their presence is very objectionable in dynamite glycerol.

Butyric acid (up to 0.5 per cent.), oxalic acid, and formic acid are also sometimes present, and may be detected by the acid nature of the sample if the glycerol has been distilled. Pure diluted glycerol should give no precipitate with a neutral solution of silver nitrate. In the presence of **formic acid**, **butyric acid**, or **acrolein**, a white precipitate is formed which blackens on standing or boiling.

French perfumers and manufacturers of cosmetics reject samples which show any change of colour or turbidity within twenty-four hours after the addition of silver nitrate.

**Rosin** is an objectionable impurity in glycerol from soap lyes, but is not present in that from candle-works. It is precipitated by lead acetate, also on acidifying. When rosin is present the distilled glycerol often has a marked fluorescence owing

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to the presence of rosin oil, which may be removed and detected by extracting with ether and evaporating.

**Specific gravity** is determined at 15° C., and may be taken in a specific gravity bottle.

**Alkalinity**, which is usually sodium carbonate and may be somewhat considerable if the soap has been grained with caustic alkali, is estimated after dilution with water by titrating with  $N/2$  acid, using methyl orange as indicator.

**Salts** are estimated by gently incinerating 5-6 g. of the glycerine, extracting the carbonaceous mass with distilled water, filtering, and evaporating the filtrate on the water bath. The dried residue represents the salts in the weight taken.

**Chloride of sodium** (common salt) is estimated by dissolving the total salts in water and titrating with  $N/10$  silver nitrate solution, using potassium chromate as indicated.

**Copper, lead, iron, magnesium, and calcium** may also be tested for in the salts in the ordinary way.

**Arsenic** is best tested for by the Gutzeit method. This is carried out by placing about 5 c.c. of the crude glycerol in a test tube, adding a few fragments of granulated zinc *free from arsenic* and then 10 c.c. of diluted HCl, and covering the tube with a piece of filter paper which has been moistened three times with alcoholic mercuric chloride solution and dried after each moistening.

If arsenic is present, a yellow stain will be observed after thirty minutes.

**Sulphates** are precipitated with barium chloride in acid solution, dried, ignited, and weighed.

**Sulphites** give with barium chloride a precipitate soluble in hydrochloric acid. If the precipitate is well washed with hot water and a few drops of iodine solution together with starch paste added, a blue starch-iodine compound first forms which gradually disappears.

**Thiosulphates** are detected by precipitating with barium chloride, filtering, acidifying, and adding a few drops of potassium permanganate solution, when the solution becomes cloudy.

**Sulphides** are tested for by replacing the mercury bichloride with lead acetate paper in the Gutzeit arsenic test. A blackening of the lead acetate paper shows the presence of sulphide.

**Sugars** may be tested for both before and after inversion by boiling with Fehling's solution.

### British Standard Specifications for Soap Lye and Saponification Crude Glycerine

The following standard specifications were drawn up by the British Executive Committee on crude glycerine analysis, and approved at a general meeting of crude glycerine makers, buyers, and brokers held in London on 3rd October 1912.

**Soap Lyes Crude Glycerine.**—Analysis to be made in accordance with the International Standards Methods, 1911 (see Chapter II.).

**Glycerol.**—The standard shall be 80 per cent. of glycerol. A crude glycerine tendered which tests 81 per cent. of glycerol or over shall be paid for at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerine which tests under 80 per cent. of glycerol but is 78 per cent. or over, shall be subject

## UNDISTILLED GLYCEROL

to a reduction of one and a half times the shortage, calculated at *pro rata* price as from 80 per cent. If the test falls below 78 per cent., the buyers shall have the right of rejection.

**Ash.**—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent. but not exceeding 10.5 per cent., a percentage deduction shall be made for the excess calculated as from 10 per cent. at *pro rata* price, and if the percentage of ash exceeds 10.5 per cent. but does not exceed 11 per cent., an additional percentage deduction shall be made equal to double the amount in excess of 10.5 per cent. If the amount of ash exceeds 11 per cent., the buyer shall have the right to reject the parcel.

**Organic Residue.**—The standard shall be 3 per cent. A percentage deduction shall be made of three times the amount in excess of the standard of 3 per cent., calculated at *pro rata* prices. The buyer shall have the right to reject any parcel which tests over 3.75 per cent.

**Saponification Crude Glycerine.**—Analysis to be made in accordance with the International Standards Methods (I.S.M.), 1911.

**Glycerol.**—The standard shall be 88 per cent. Any crude glycerine tendered which tests 89 per cent. or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 88 per cent. Any crude glycerine which tests under 88 per cent. but is 86 per cent. or over, shall be subject to a reduction of one and a half times the shortage, calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent., the buyer shall have the right of rejection.

Thus, any premium to be paid would be based upon the price per unit of glycerol, e.g., an excess of 1.0 per cent. in the glycerol content above the standard of 88 per cent. would mean an additional  $\frac{1}{88}$  on the contract price, and a deficiency of 1.0 per cent. in the glycerol content would mean a deduction of  $\frac{1.5}{88}$  on the contract price. For example of calculation, see Soap Lyes Crude.

**Ash.**—The standard shall be 0.5 per cent. In the event of the percentage of ash exceeding 0.5 per cent., a percentage deduction shall be made equal to double the amount in excess of the standard of 0.5 per cent. calculated at contract price. If the amount of ash exceeds 2.0 per cent. the buyer shall have the right to reject the parcel.

Example :—

Let D = Deduction from contract price due to excess over the standard (0.5 per cent.).

Z = Contract price, say £68 per ton.

e = Excess of ash over the standard (0.5 per cent.).

Then 
$$D = \frac{Z \times 2e}{100}$$

Therefore if analysis shows 1.20 per cent. ash,

$$D = \frac{68 \times 0.7 \times 2}{100} = 19s. \text{ per ton.}$$

**Organic Residue.**—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent. calculated at contract price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

The example and formula for ash as above is equally applicable to organic residue.

## CHAPTER IV

## DISTILLED GLYCEROL—SPECIFICATIONS FOR CHEMICALLY PURE GLYCEROL

## Distilled and Dynamite Glycerol

**Distilled Glycerol**, obtained as previously described above, by distilling crude glycerol, varies in colour from **yellow** to **nearly white**. The specific gravity varies from 1.22-1.26.

**Chemically pure** glycerol is sold in *three grades*, sp. gr. 1.24, sp. gr. 1.25, and sp. gr. 1.26, and should be water-white.

The percentage of glycerol is easiest to determine by the specific gravity test (detailed below), and also by determining the refractive index, tables for which are given in Chapter I.

The following are the usual requirements of chemically pure glycerol :—

**Ash** and **polyglycerol** together should not exceed 0.03 per cent. **Ash** alone should not exceed 0.01 per cent.

**Acrolein** and other reducing substances should cause no reduction of silver nitrate after standing for twenty-four hours.

**Fatty acids** should be tested for (see pp. 24, 26 below).

**Arsenic** must not exceed 1 part in 250,000. It may be estimated by the Gutzeit test, described in Chapter III. above. The **electrolytic method**, however, is now in general use.

**Sulphuric Acid Test**.—Pure glycerol should not acquire a yellow or brown colour when very gradually mixed with an equal volume of **cold concentrated sulphuric acid**. In the presence of **sugar** a darkening or charring occurs. **Oxalic** or **formic acid** may cause effervescence when warmed. **Oxalic acid** is more readily detected by the white precipitate formed when calcium acetate is added to the diluted sample.

**Fehling Solution Test**.—Pure glycerol does not reduce Fehling solution when heated to 100° C. with it for a few minutes, although prolonged boiling causes a precipitate.

In the presence of **dextrose** and **arsenious acid** reduction occurs before the boiling point is reached.

To detect **cane sugar** dilute the sample to five times its volume with water, add half its volume of concentrated HCl, and heat to 70°-80° C. for ten minutes, when the cane sugar is hydrolysed. Neutralise exactly with NaOH and then heat to 100° C. with the Fehling solution, when a red precipitate is immediately produced.

*British Pharmacopœia*, 1914.—The following are the requirements for  
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chemically pure **glycerinum**, **glycerine**, or **glycerol**: Sp. gr. 1.260. Neutral to litmus. An aqueous solution (1 in 10) yields no characteristic reaction for ammonium compounds, chlorides, or sulphates. Assumes when heated not more than a faint yellow but no pink coloration, and yields not more than a very slight charred residue and no odour of burnt sugar (absence of *sugar*); undergoes no darkening in colour when mixed with an equal volume of solution of ammonia and a few drops of solution of silver nitrate, the mixture being kept protected from light and the observations made after the lapse of five minutes (absence of *formic acid* and *acrolein*). Gently warmed with an equal volume of diluted sulphuric acid, the mixture being vigorously shaken, not more than a faint odour is noticeable (absence of *fatty acids*). Shaken with an equal volume of sulphuric acid, the mixture being kept cool, not more than a very slight straw coloration is produced (absence of *extraneous organic matter*). A mixture of 10 c.c. of glycerine with 40 c.c. of water, 1 drop of solution of ammonia and 1 drop of solution of tannic acid assumes not more than a faint and transient pink or purple coloration (limit of *iron*). When tested for lead according to the quantitative test described in the B.P., Appendix V., but using 10 g. in each Nessler glass, no difference is observed upon the addition of the solution of sodium sulphide to one of the solutions (absence of *lead*); when the foregoing test is repeated, but omitting the addition of solution of ammonia and of solution of potassium cyanide and adding to each solution 1 c.c. of diluted hydrochloric acid, no difference in colour is observed upon the addition of solution of hydrogen sulphide to one of the solutions (absence of *copper*). Arsenic limit, 2 parts per million. No appreciable ash.

*U.S.A. Pharmacopœia*, 1916.—The **glycerinum** of the U.S.A. Pharmacopœia must fulfil the following requirements:—

It is made by the hydrolysis of vegetable or animal fats or fixed oils, is purified by distillation, and must contain not less than 95 per cent. of glycerol,  $C_3H_8(OH)_3$ .

*Glycerine* is a clear, colourless liquid, of a thick syrupy consistency, having not more than a slight characteristic odour which is neither harsh nor disagreeable, sweet to the taste, and producing a sensation of warmth in the mouth; when exposed to the air it absorbs moisture.

Glycerine is miscible with water or alcohol; insoluble in chloroform, ether, benzene, petroleum benzin, carbon disulphide, or fixed or volatile oils.

An aqueous solution of glycerine (1 in 20) is neutral to litmus.

Specific gravity: not below 1.249 at 25° C.

Glycerine does not appreciably volatilise from weak aqueous solutions. When of a strength between 70 and 100 per cent., it rapidly volatilises at 100° C.

When a few drops of glycerine are heated with about 0.5 g. of potassium bisulphate, pungent vapours of acrolein are evolved.

Glycerine is colourless when viewed transversely in a tube of colourless glass about 30 mm. in diameter, held in a vertical position.

When 50 g. of glycerine is heated in an open, shallow, 100 mil<sup>1</sup> porcelain or platinum dish until it ignites, and then is allowed to burn without further application of heat in a place free from draught, not more than 0.015 per cent. of carbonaceous and mineral residu remains. When this residu is subjected to a low red heat until combustion is complete, not more than 0.007 per cent. of mineral ash remains; when this ash is dissolved in 10 mls (10 c.c.) of distilled water and titrated with N/100 silver nitrate V.S., using potassium chromate T.S. as indicator, then in the original 50 g. of glycerine there must not be more than 0.001 per cent. of chlorides, calculated as sodium chloride. Each mil (1 c.c.) of N/100 silver nitrate V.S. consumed corresponds to 0.0005846 g. of NaCl.

When 5 mls (5 c.c.) of glycerine are mixed by vigorous shaking with an equal

<sup>1</sup> 1 mil = 1/1,000 of a litre = about 1 c.c.

volume of sulphuric acid in a glass-stoppered cylinder, the liquid does not become darker than yellow on standing for one hour (*readily carbonisable impurities*).

When 50 g. of glycerine are mixed with 50 mls (50 c.c.) of freshly boiled distilled water and 5 mls (5 c.c.) of N/2 potassium hydroxide V.S., and the mixture is boiled for *five minutes*, when cold the liquid requires not less than 4 mls (4 c.c.) of N/2 hydrochloric acid V.S. for neutralisation, using phenolphthalein T.S. as indicator (*fatty acids and esters*).

An aqueous solution of *glycerine* (1 in 10) remains clear on the addition of calcium chloride T.S. (oxalic acid); another portion of the solution is not affected by barium chloride T.S. after acidulation with a few drops of diluted hydrochloric acid (sulphate).

An aqueous solution of glycerine does not respond to the test for *heavy metals* as described in Part II., Test No. 3, of the U.S. Pharmacopœia.

This test consists in acidulating 10 mls (c.c.) of a solution of glycerol in distilled water (1 in 50), contained in a test tube of about 40 mls (c.c.) capacity and of about 2.5 cm. in diameter, with 1 ml (1 c.c.) of diluted hydrochloric acid, warming it to 50° C., adding an equal volume of freshly prepared hydrogen sulphide T.S., closing the tube with a stopper, and allowing the mixture to stand at 35° C. for half an hour. At the end of this time the mixture should still possess the odour of hydrogen sulphide, if not it should be thoroughly saturated with the gas and again set aside for half an hour. The colour produced, if any, is not greater than that observed by a blank test made in the same manner and with the same quantities of reagents (omitting the solution to be tested); the solutions are viewed cross wise by reflected light while held against a white surface. A slight turbidity due to the separation of sulphur from the hydrogen sulphide may occur.

An aqueous solution of glycerine must meet the requirements of the test for arsenic as described in Part II., Test No. 1, of the U.S. Pharmacopœia.

This means not more than 1 part of arsenic in 100,000 of the substance tested.

A mixture of 5 mls (5 c.c.) of glycerine and 5 mls (5 c.c.) of an aqueous solution of potassium hydroxide (1 in 10) does not become yellow when kept for five minutes at 60° C. (*acrolein, glucose*), nor emit an odour of ammonia (*ammonium compounds*).

## CHAPTER V

# DISTILLED GLYCEROL—SPECIFICATIONS FOR DYNAMITE GLYCEROL

**Dynamite glycerol** is distilled glycerol having sp. gr. 1.261 and above. The colour varies from light yellow to deep yellow. The specific gravity must not be less than 1.261 at 15.5° C. **Lime, magnesia, and alumina** should be absent. **Chlorides** must be present only as traces. 2 c.c. of silver nitrate diluted with 1 c.c. of glycerol should yield only a faint turbidity.

**Arsenic** should be present only in traces. The Gutzeit test is too delicate. Hence test by making the glycerol only **very faintly** alkaline with ammonia. Next add silver nitrate. No milkiness should be visible. Excess of ammonia spoils the test, since silver arsenite is soluble therein.

**Organic Impurities.**—Dilute 1 c.c. of the glycerol with 2 c.c. of water and mix with a 10 per cent. solution of silver nitrate. No black or brown colour within ten minutes should be visible.

**Ash** must not exceed 0.15 per cent.

**Free Acid.**—The sample must not redden blue litmus paper. Detect volatile fatty acids by warming with alcohol and concentrated sulphuric acid; a fruity odour (equals fatty acid esters) shows their presence. 1 c.c. diluted with 2 c.c. of water should yield no precipitate with concentrated HCl.

**Nitration Test.**—In order to see whether a sample is really suitable for the manufacture of dynamite it is advisable to nitrate a sample under conditions which imitate those obtaining on the large scale, since cases have been known where samples of glycerol answer all the preceding tests and yet are unsuitable for actual manufacturing operations on the large scale.

As this is a dangerous experiment it should be attempted only by experienced operators. Many chemists diminish the amount of glycerol to 15 g. (which is the smallest quantity which can be used for this test), but the usual practice is to use 50 g. The operation is carried out as follows<sup>1</sup>:—

Mix together and cool in a stoppered vessel a mixture of 1 part by weight of fuming nitric acid (sp. gr. 1.5) and 2 parts of pure sulphuric acid (sp. gr. 1.845).

Place 375 g. of the mixed acid into a thin walled beaker of 500 c.c. capacity, and standing in a large vessel through which a constant current of cold water passes.

The leading tube must be firmly fixed both to the tap and basis, since should it come loose and water splash into the beaker during the operations an explosion may ensue.

<sup>1</sup> See *Lewkowitsch, Jour. Soc. Chem. Ind.*, 1895, 1073. Also his "Chemical Technology of Oils, Fats, and Waxes," 6th Edition, vol. iii., p. 394.

Now weigh out 50 g. of the glycerol and add drop by drop to the mixed acid in the beaker, using a thermometer as stirrer.

The mixed acid should be at an initial temperature of  $12^{\circ}$ - $15^{\circ}$  C. The stirring must be very thorough to avoid local heating. The temperature must not increase beyond  $30^{\circ}$  C.,  $25^{\circ}$  C. being a safer limit.

If the temperature indicates danger, instantly perforate the bottom of the beaker with a thermometer and so drown the contents in the mass of water.

When the temperature has fallen to  $15^{\circ}$  C., run the liquid into a perfectly dry separating funnel, which has been previously rinsed out with strong sulphuric acid.

The more rapidly the liquids separate and the sharper the line of demarcation between the nitroglycerol and the acids, the better is the glycerol. Although the nitroglycerine formed will always be turbid, yet if (a) it contains flocks; (b) the separation is not complete in five or ten minutes; (c) if there is a cloudy middle layer of liquid, **the glycerol must be rejected.**

With very bad samples no separation at all may be obtained on standing many hours. This test may be made quantitative by running off the acids, carefully giving the nitroglycerine a slight rotatory motion in the separator in order to detach drops of acid from the walls (but not *shaking* the nitroglycerine), washing with warm water ( $35^{\circ}$ - $40^{\circ}$  C.), and once or twice with caustic soda (20 per cent.) solution, and again with water.

The liquid is now run into a 100 c.c. burette, and when the excess of water has risen to the top, the volume of the nitroglycerine is read off. This multiplied by 1.6 gives its weight. The yield should be 207-210 per cent. (*Theory*, 246.7).

To destroy the nitroglycerine absorb in a thin layer of sawdust spread in an open yard away from buildings. Then set on fire with a match. It burns away quietly.

As regards the danger of using unsuitable glycerol for dynamite making, see *O. Guttman*, *Jour. Soc. Chem., Ind.*, 1892, p. 207; *G. E. Barton*, *Jour. Amer. Chem. Soc.*, 1895, 17, 277; *Lewkowsitch*, *Chem. Zeit.*, 19, 1423; *Jour. Soc. Chem. Ind.*, 1895, 1073.

As regards the specifications required for refined glycerol by the Explosives Companies, see Chapter VIII.

The following is a specification for dynamite glycerine as stipulated by a well-known explosives company:—

**Specific Gravity.**—The specific gravity is to be not less than 1.262 at

$15.5^{\circ}$  C.  
 $15.5^{\circ}$  C.

**Reaction.**—The glycerine is to be neutral to litmus.

**Colour and Smell.**—The glycerine is to be light in colour, and must emit no unpleasant smell when heated to  $100^{\circ}$  C.

**Glycerol.**—The glycerine is to contain not less than 98.5 per cent. of glycerol, determined by the Acetin Method, described on pp. 9-11 of the "International Standards Methods, 1911," for crude glycerine.

**Moisture.**—The glycerine is to contain not more than 1.5 per cent. of moisture, determined by the method described on p. 8 of the "International Standards Methods, 1911," for crude glycerine.

**Chlorides.**—The glycerine is not to contain more than 0.01 per cent. of chlorides calculated as NaCl.

**Ash.**—The ash is not to exceed 0.05 per cent.

**Ammoniacal Silver Nitrate Test.**—When 10 c.c. of a 10 per cent. solution of the glycerine are mixed with 10 c.c. of a 10 per cent. solution of ammonia, and 10 c.c. of a 10 per cent. solution of silver nitrate added, and the mixed solution is heated to  $60^{\circ}$  and then allowed to stand in the dark for 10 minutes, there must be no apparent reduction of the silver.

**Saponification Equivalent.**—The saponification equivalent of the glycerine, determined as follows, is not to exceed 0.1 per cent.  $\text{Na}_2\text{O}$ :—100 g. of the sample are weighed out into a flask, 3 c.c. of normal sodium hydroxide and 200 c.c. of boiling water free from  $\text{CO}_2$  added, the flask tightly corked, placed on top of a boiling water oven for one hour, cooled, and the excess of alkali titrated back with normal acid, phenolphthalein being used as indicator.



A. H. Salway (*Jour. Soc. Chem. Ind.*, 1918, 37, 126 T.) made an examination of the impurities in glycerol from whale oil, with reference to the suitability of such glycerol for the production of dynamite. His conclusions are as follows :—

(1) The best varieties of whale oil (No. 0) yield glycerine equal in quality to that from vegetable oils, and may therefore be safely used for the manufacture of dynamite glycerine.

(2) Medium quality whale oils (Nos. 1-3) yield distilled glycerine containing minute quantities of trimethyleneglycol and nitrogenous matter. The amount of impurity is, however, too small to affect the glycerine deleteriously.

(3) Very inferior whale oils (No. 4 quality) are unsuitable for the production of dynamite glycerine, and should be rejected. Such oils may be recognised by their high nitrogen content and high percentage of free fatty acid, and by the fact that distilled glycerine prepared from them gives a precipitate with phosphotungstic acid in the presence of 5 per cent. sulphuric acid. In general, if a sample of glycerine responds to the latter test, it should be rejected.

Previous failures in the use of whale oil glycerol for dynamite manufacture (see *Jour. Soc. Chem. Ind.*, 1911, 30, 984) are thus explained.

## CHAPTER VI

# DISTILLED GLYCEROL—PREPARATION OF THE SAMPLE OF REFINED GLYCEROL FOR ANALYSIS

### LITERATURE

COMBY and BACKUS. *Jour. Ind. and Eng. Chem.*, 1910, 2, 14.  
ALLAN'S "Commercial Analysis," vol. ii., Art. by Dr Lawrie.

**Preparation of the Sample of Refined Glycerol for Analysis.**—The glycerol often arrives at the works in car loads of about thirty drums. A composite sample should be made for each five drums of a shipment (unless a special sample of each drum is required).

The **sample bottles** are wide-mouthed and glass-stoppered, of at least 800 c.c. capacity.

The bottles and corresponding stoppers are all marked so that the stoppers will be returned to the proper bottles after washing and drying, thus ensuring tightly stoppered vessels.

Immediately before use the bottles are thoroughly dried with alcohol ether, followed by a stream of dry air; or they are placed in a hot air oven some time before use. After drying, the stoppers are inserted.

The **sampling instrument** (called a "thief") has been described on p. 9 under **crude glycerol**. In many works, however, a piece of glass tubing is employed, about 2 cm. internal diameter and 70 cm. in length, delivering from 125-150 c.c. of glycerol. One end is partially closed up, leaving an air hole which can be easily covered by the thumb. One "thief" full from each drum is taken, the wide diameter of the tube ensuring rapid delivery and thus exposing the glycerol for as short a time as possible to the atmosphere.

This is important, as glycerol is very hygroscopic and rapidly absorbs water from the air.

To take the sample the "thief" is lowered into the glycerol drum only very slowly, so that the full "thief" represents a sample drawn from each section of the drum.

If lowered rapidly to any one point and kept there, obviously only the glycerol about that point will flow into the instrument and thus only a local sample will be obtained.

When the "thief" is full, withdraw rapidly, pulling it through one hand tightly clasped around it so as to strip it of the adhering outer coating of viscid glycerol, and allow the drippings to flow back into the drum. Then smartly transfer the "thief" full of glycerol to the sample bottle. In sampling a new drum rinse the "thief" at least twice in the glycerol contained therein before taking the actual sample.

Immediately after allowing the glycerol to enter the sampling bottle, wipe with a dry cloth any glycerol from the outside of the neck and stopper of the sample bottle, thus preventing the danger of glycerol between the neck and stopper from absorbing moisture from the air on standing. Each filled sample bottle (representing five drums) is now allowed to stand until all air bubbles disappear.

If there is any necessity to transfer glycerol from the original bottle to another, always take care to carefully wipe the lip, inside the neck, and stopper of the bottle with a dry cloth both before and after pouring out the glycerol, so that if perchance any glycerol adhering to the stopper has taken up moisture on standing, none of this diluted glycerol will get into the sample taken for examination.

## CHAPTER VII

# DISTILLED GLYCEROL—METHOD OF ESTIMATING ITS SPECIFIC GRAVITY

### LITERATURE

A. M. COMEY and C. F. BACKUS. *Jour. Ind. and Eng. Chem.*, 1910, 2, 11.

"Ardeer Factory Analytical Method Book," Part II. A, Method No. 33.

J. W. LAWRIE. Allan's "Commercial Analysis," 5th Edition, 1924, vol. ii., p. 702.

THE following is an outline of the method of control used in the American E. I. du Pont de Nemours Powder Factory and at the Ardeer Factory of Nobel's Explosive Works in Scotland.

The methods, therefore, represent the highest degree of accuracy consistent with technical work and are based on a manufacturing experience extending over fifteen years.

**Specific Gravity Test.**—This is one of the most important tests for the purity of glycerol. Duplicate estimations should agree to within 0.00005 in the actual specific gravities. Two different workers should agree to  $\pm 0.00015$  in the specific gravity of the same sample. Hence extreme care is necessary in carrying out the determination.

The hydrometer cannot be used for determining the specific gravity of glycerol, as it is far too viscid to make the readings reliable. A specific gravity bottle or a pycnometer must be employed.

One type of **pycnometer** often used is shown in Fig. 2, consisting of the standard 50 c.c. Geissler type, fitted with a very accurate thermometer calibrated at 15°, 20°, 25°, and 30° C., each instrument being provided with thermometric corrections for these four temperatures.

The disadvantages presented by this type of instrument are: (1) The soft glass used in manufacture has a high coefficient of expansion (0.000025 per 1° C. between 15.6° and 30° C.), and chips easily on usage and on grinding; (2) the thermometers in the stopper are never accurate enough for use in determining the specific gravity of refined glycerol, and usually only approximations of the true temperature of the glycerol inside the pycnometer are possible; (3) the final temperature is best arrived at by an external accurate thermometer placed in the constant water bath in which the pycnometer is immersed for a sufficient time for the glycerol to attain this same temperature throughout, so that the thermometer in the stopper is a needless complication.

A better type of pycnometer is that designed by *Walker* (109, U.S. Bureau of Chemistry), which is shown in Fig. 3. Here the thermometers in the stem are dispensed with and the apparatus is made of hard *pyrex* glass.

The coefficient of cubical expansion of *pyrex* glass is only 0.000008 per 1° C., which thus reduces to a minimum errors due to expansion of the glass apparatus.

**Best Temperature for Carrying Out the Estimation.**—The specific gravity required is defined as:—

$$\text{Specific gravity at } 15.6^\circ \text{ C.} = \frac{\text{Weight in grams of a given volume of glycerol at } 15.6^\circ \text{ C.}}{\text{Weight of the same volume of water at } 15.6^\circ \text{ C.}}$$

But matters are complicated by the fact that it is difficult in practice to carry out the measurements at 15.6° C.

(1) The average temperature of the air may be considerably above  $15.6^{\circ}\text{C.}$ , and so moisture might deposit on the cold pycnometer, rendering inevitable a delay in weighing until equilibrium with the atmosphere was reached.

(2) It may be difficult to keep the constant temperature bath exactly at  $15.6^{\circ}\text{C.}$ , but it is always easy to keep it constant at some temperature ( $^{\circ}\text{C.}$ ) approximating to that prevailing in the laboratory at the time. For example, if the laboratory temperature be  $26^{\circ}\text{C.}$  the evaporation of the water in the bath will cause its temperature to remain nearly constant at  $24^{\circ}\text{C.}$ ; so that in this particular case specific gravity is most easily measured at  $24^{\circ}\text{C.}$  and not at  $15.6^{\circ}\text{C.}$

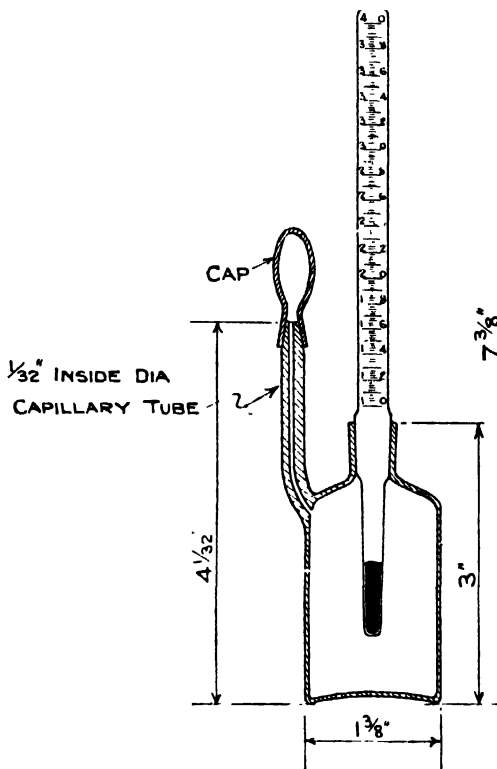


FIG. 2.—Geissler Pycnometer for Determining the Specific Gravity of Glycerol.

The estimations, therefore, are made always at that temperature at which the bath is most easily kept constant, provided that this temperature lies between  $15.6^{\circ}$  and  $30^{\circ}\text{C.}$  ( $60^{\circ}$ - $80^{\circ}\text{F.}$ ).

**Determination of the Weight of Water held by the Pycnometer at  $15.6^{\circ}\text{C.}$  ( $60^{\circ}\text{F.}$ ).**—Clean the interior of the pycnometer with bichromate cleansing mixture, rinse thoroughly with water, alcohol, and ether, and dry by forcing or sucking through a current of air which has passed a drying train. Now wipe with a damp and then with a dry cloth or with filter paper, and weigh.

This treatment frees the pycnometer from acid, dust, and grease, and ensures uniformity with respect to the invisible film of moisture (present on all glass services), thus enabling accurate weighings to be carried through rapidly. It is especially important that the pycnometer should never have its temperature considerably increased before a determination, as all kinds of complications are thereby introduced.

Boil some distilled water and cool to about the temperature of the constant temperature bath.

Fill the pycnometer with this water by means of a piece of glass tubing 6 cm. long attached to the capillary tube of the pycnometer by a small piece of rubber

tubing 2 cm. long by 2.5 mm. diameter; suck the water well up the capillary tube..

Take care to avoid the introduction of air bubbles. After filling, insert the stopper and place in the constant water bath until the thermometer in the pyknometer and that in the bath register the same temperature. Give ten minutes further time for safety.

Remove tubing attachment and wipe away excess water from top of capillary tube with a dry finger. Remove pyknometer from the water bath, wipe ground portion of capillary quickly with a piece of filter paper, and replace cap tightly.

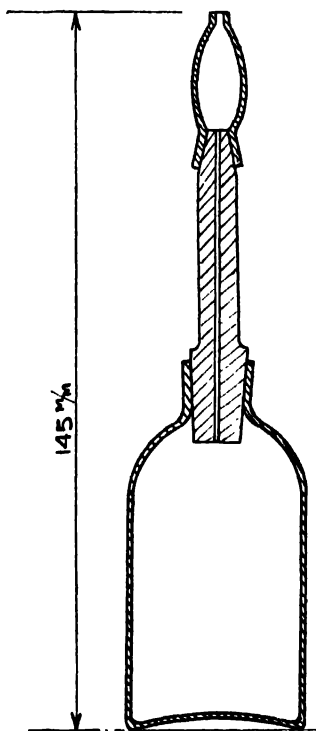


FIG. 3.—Walker's Pyknometer for the Specific Gravity of Glycerol.

Wipe whole pyknometer first with a wet cloth and then with a dry cloth, and weigh rapidly.

Then 
$$C = W \cdot \frac{D}{d} \cdot \frac{1}{1 + a(t - 15.6)} \quad (1)$$

Where  $C$  = Number of grams of water which fill the pyknometer at  $15.6^\circ \text{C}$ .

$W$  = Number of grams of water which fill the pyknometer at the temperature of the water bath  $t^\circ \text{C}$ .

$D$  = Density of water at  $15.6^\circ \text{C}$ . = weight in grams of 1 c.c.

$d$  = Density of water at  $t^\circ$ , the temperature of water bath.

$a$  = Coefficient of cubical expansion of the glass of which the pyknometer is made.

$a = 0.000025$  per  $1^\circ \text{C}$ . for ordinary soft pyknometer glass, and  $0.000008$  for pyrex glass.

*Proof of Formula (1).*—If  $V$  be the volume in cubic centimetres of the pyknometer at  $15.6^\circ$ , then number of grams of water contained in the bottle at  $15.6^\circ$  is :—

$$C = V \times D, \text{ or } V = \frac{C}{D} \quad (2)$$

But at  $t^\circ$  the volume of the bottle becomes  $V[1 + \alpha(t - 15.6)]$ , and the weight of water it now contains is :—

$$W = d \times V[1 + \alpha(t - 15.6)],$$

or

$$V = \frac{W}{d[1 + \alpha(t - 15.6)]} \quad (3)$$

From equations (2) and (3) :—

$$V = \frac{C}{D} = \frac{W}{d} \cdot \frac{1}{[1 + \alpha(t - 15.6)]},$$

or

$$C = W \cdot \frac{D}{d} \cdot \frac{1}{1 + \alpha(t - 15.6)} \quad (4)$$

which is the required formula.

The values of  $D$  and  $d$  can be read off from the following table :—

### Specific Gravity Calculations

TABLE I.—DENSITY OF PURE WATER FREE FROM AIR  
VALUES OF  $D$  AND  $d$

° C.	Tenths of Degrees.										Mean Differences.
	0	1	2	3	4	5	6	7	8	9	
0	0.9998681	8447	8812	8875	8936	8996	9053	9109	9163	9216	+ 59
1	9267	9315	9363	9405	9452	9494	9534	9573	9610	9645	+ 41
2	9679	9711	9741	9769	9796	9821	9844	9866	9887	9905	+ 24
3	9922	9951	9962	9973	9981	9988	9994	9998	9998	0000	+ 8
4	1.0000000	9999	9996	9992	9986	9979	9970	9960	9947	9934	- 8
5	0.9999999	9902	9884	9864	9842	9819	9795	9769	9742	9713	- 24
6	9682	9650	9617	9582	9545	9507	9468	9427	9385	9341	- 39
7	9296	9249	9201	9151	9100	9048	8994	8938	8881	8823	- 53
8	8764	8703	8641	8577	8512	8445	8377	8308	8237	8165	- 67
9	8091	8017	7940	7863	7784	7704	7622	7539	7455	7369	- 81
10	7282	7194	7105	7014	6921	6826	6729	6632	6533	6432	- 95
11	6331	6228	6124	6020	5913	5805	5696	5586	5474	5362	- 108
12	5248	5132	5016	4898	4780	4660	4538	4415	4291	4166	- 121
13	4040	3912	3784	3650	3523	3391	3257	3122	2986	2859	- 133
14	2712	2572	2431	2289	2147	2003	1858	1711	1564	1416	- 145
15	1266	1114	0962	0809	0655	0499	0343	0185	0026	9865	- 156
16	0.9989705	9542	9378	9214	9048	8881	8713	8544	8373	8202	- 168
17	8029	7856	7681	7505	7328	7150	6971	6791	6610	6427	- 178
18	6244	6058	5873	5686	5498	5309	5110	4927	4735	4541	- 190
19	4347	4152	3955	3757	3558	3358	3158	2955	2752	2549	- 200
20	2343	2137	1930	1722	1511	1301	1090	0878	0663	0449	- 211
21	0233	0016	9799	9580	9359	9139	8917	8694	8470	8245	- 221
22	0.9978019	7792	7564	7335	7104	6873	6641	6408	6173	5938	- 232
23	5702	5466	5227	4988	4747	4506	4264	4021	3777	3531	- 242
24	3286	3039	2790	2541	2291	2040	1788	1535	1280	1026	- 252
25	0770	0513	0255	9997	9736	9476	9214	8951	8688	8423	- 261
26	0.9968158	7892	7624	7356	7087	6817	6545	6273	6000	5726	- 271
27	5451	5176	4898	4620	4342	4062	3782	3500	3218	2925	- 280
28	2652	2366	2080	1793	1505	1217	0928	0637	0346	0053	- 289
29	0.9959761	9466	9171	8876	8579	8282	7983	7684	7383	7083	- 298
30	6780	6478	6174	5869	5564	5258	4950	4642	4334	4024	- 307
31	3714	3401	3089	2776	2462	2147	1832	1515	1198	0880	- 315
32	0561	0241	9920	9599	9276	8954	8630	8304	7979	7653	- 324
33	0.9947325	6997	6668	6333	6007	5676	5345	5011	4678	4343	- 332
34	4007	3671	3335	2997	2659	2318	1978	1638	1296	0953	- 340
35	0610	0267	9922	9576	9230	8883	8534	8186	7837	7486	- 347
36	0.9937136	6784	6432	6078	5725	5369	5014	4658	4301	3943	- 355
37	3585	3226	2866	2505	2144	1782	1419	1055	0691	0326	- 362
38	0.9929960	9593	9227	8859	8490	8120	7751	7380	7008	6636	- 370
39	6263	5890	5516	5140	4765	4389	4011	3634	3255	3876	- 377
40	2497	2116	1734	1352	0971	0587	0203	9818	9433	9047	- 384
41	0.9918661	...	...	...	...	...	...	...	...	...	...

## DISTILLED GLYCEROL

**Determination of the Weight of Glycerol held by the Pyknometer at 15.6° C.**—(a) Empty the pyknometer of the distilled water, rinse with alcohol and ether as before, and expel the ether by sucking through air which has passed through a drying train.

(b) Place tubing attachment firmly over end of pyknometer capillary as before in determining the water capacity, and fill apparatus with glycerol from a sample bottle, avoiding any air bubbles.

In order to avoid diluted glycerol entering the apparatus, wipe the lip and inside of the neck of the sample bottle with a clean dry cloth both before and after pouring out the glycerol. Also wipe the stopper of the sample bottle before replacing it.

(c) After filling the pyknometer draw the glycerol well up the capillary tube by means of the rubber attachment, place the thermometer in position, wash the whole free from surplus glycerol, and place in the water bath for ten minutes longer than the time required for the pyknometer thermometer to register the same temperature as the water bath thermometer.

(d) Remove the rubber tubing from the capillary, wipe with a dry finger the surplus glycerol from the top of capillary, remove the pyknometer from the water bath, wipe the ground portion of the capillary quickly with a piece of filter paper, and replace the cap firmly. Wipe the whole apparatus first with a wet cloth, then with a dry cloth, and weigh rapidly.

Then 
$$S = \frac{G}{C} \cdot \frac{1 + B(t - 15.6)}{1 + \alpha(t - 15.6)} \quad (4)$$

Where  $S$  = Specific gravity of the glycerol at 15.6° C./15.6° C.

$t$  = Temperature degree of constant water bath in degrees centigrade.

$G$  = Number of grams of glycerol contained in the pyknometer at  $t^\circ$  C.

$C$  = Number of grams of water contained in the pyknometer at 15.6° C. (as previously determined).

$\alpha$  = Thermal coefficient of cubical expansion of the glass, which amounts to 0.000025 per 1° C. for soft glass, or 0.000008 per 1° C. for pyrex glass.

$B$  = Thermal coefficient of cubical expansion of glycerol = 0.000610 between 15.6° and 20° C.; 0.000615 between 20° and 25° C.; 0.00062 between 25° and 30° C.

*Proof of Formula (4).*—The volume of the glass pyknometer at  $t^\circ$  is  $V[1 + \alpha(t - 15.6)]$  c.c. Hence if 1 c.c. of glycerol weighs  $x_t$  g. at  $t^\circ$ , the weight of glycerol contained in the bottle at  $t^\circ$  is—

$$G = x_t \cdot V \cdot [1 + \alpha(t - 15.6)] \text{ g.,}$$

or 
$$V = \frac{G}{x_t[1 + \alpha(t - 15.6)]} \text{ c.c.} \quad (1)$$

But at 15.6° C. the volume of the glass bottle is  $V$  c.c., so that if 1 c.c. of glycerol at 15.6° C. weighs  $x_{15.6}$  g., then if

$$M = \text{Weight of } V \text{ c.c. of glycerol at } 15.6^\circ \text{ C.,}$$

then 
$$M = V \times x_{15.6} \text{ g.} \quad (2)$$

Substituting the value of  $V$  from (1),

$$M = \frac{x_{15.6}}{x_t} \cdot G \cdot \frac{1}{1 + \alpha(t - 15.6)} \quad (3)$$

If the coefficient of cubical expansion of the glycerol be  $B$ , then 1 c.c. of glycerol at 15.6° C. (and weighing  $x_{15.6}$  g.) becomes  $[1 + B(t - 15.6)]$  c.c. when heated to  $t^\circ$  C.

or  $1 + B(t - 15.6)$  c.c. of glycerol at  $t^\circ$  C. weighs  $x_{15.6}$  g.,

or 1 c.c. of glycerol at  $t^\circ$  C. weighs  $\frac{x_{15.6}}{1 + B(t - 15.6)}$  g.,

or 
$$x_t = \frac{x_{15.6}}{1 + B(t - 15.6)}$$

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Substituting this value of  $x_t$  in (3) we have—

$$M = \frac{1 + B(t - 15.6)}{1 + a(t - 15.6)} \cdot G.$$

But specific gravity of glycerol required is :—

$$\begin{aligned} &= \frac{\text{Weight of V c.c. of glycerol at } 15.6^\circ \text{ C.}}{\text{Weight of V c.c. of water at } 15.6^\circ \text{ C.}} \\ &= \frac{M}{C} = \frac{1 + B \cdot (t - 15.6)}{1 + a(t - 15.6)} \cdot \frac{G}{C}. \end{aligned}$$

In determining the purity of the glycerol, use the *Ardeer* Table, p. 5, Section IV.

*Comey* and *Backus* (*Jour. Ind. and Eng. Chem.*, 1910, **2**, 14) calculate the specific gravity of glycerol at  $15.6^\circ \text{ C.}$  when determined at  $t^\circ$  centigrade from the formula :—

$$\text{Specific gravity at } \frac{15.6^\circ}{15.6^\circ} = \frac{W}{C} \cdot \frac{1}{1 + a(t - 15.6)} + B(t - 15.5)$$

in which  $W$  = Weight of glycerol at  $t^\circ \text{ C.}$

$C$  = Capacity of pyknometer in grams of water at  $15.6^\circ \text{ C.}$

$a$  = Thermal coefficient of expansion of glass = 0.000025 for  $1^\circ \text{ C.}$

$B$  = Thermal coefficient of expansion of glycerol = 0.000612 at  $20^\circ \text{ C.}$ ,  
0.000617 at  $25^\circ \text{ C.}$ , 0.000622 at  $30^\circ \text{ C.}$

$t$  = Observed temperature at which the determination is carried out.

This formula is also used in Allan's "Commercial Analysis."



## CHAPTER VIII

## DISTILLED GLYCEROL—METHODS FOR ITS CHEMICAL EXAMINATION

**Chemical Tests for Pure Glycerol.**—The following are the methods employed by explosive works for testing the purity of distilled glycerol.

(1) **Acidity or Alkalinity.**—Fifty c.c. of the glycerol, contained in a measuring cylinder, are poured into a beaker and the cylinder is washed out with 100 c.c. of distilled water containing 0.5 c.c. phenolphthalein indicator rendered exactly neutral by acid or alkali.

Then titrate the glycerol solution to exact neutrality, using 0.3 N.NaOH or 0.3 N.HCl as required.

Express the results as the number of cubic centimetres of N.NaOH or N.HCl required per 50 c.c.

Many samples of distilled glycerol are slightly acid owing to the presence of minute traces of *resin acids* and, less frequently, *fatty acids*.

A very delicate test for *fatty acids* is the *camphor test* (see J. W. Lawrie, Allan's "Commercial Analysis," 5th Edition, 1924, vol. ii., p 702), which is carried out by placing 200 c.c. of very pure distilled water in a beaker absolutely free from all traces of grease. Next add a fragment of camphor about the size of a pin head. The camphor acquires a rotary motion. Now add a few cubic centimetres of the diluted glycerol to be tested. If either animal or vegetable fatty acids or greases are present, the rotatory movement of the camphor ceases and it floats quietly on the surface. Mineral oils are without action. Owing to the sensitiveness of the test, extreme cleanliness is essential; even such a small amount of fat as is obtained by drawing the finger through the hair and dipping it in the water will arrest the motion of the camphor.

(2) **Ash.**—Fifty grams of the glycerol are weighed into a tared platinum dish and heated until the vapours burn after the removal of the flame.

Cool in a desiccator and weigh the "*char*."

The operation must be carried out in a place free from draughts, otherwise the burning glycerol may be prematurely extinguished, thereby lessening the degree of carbonisation of the residue, which consists mainly of carbon together with a little incompletely carbonised organic matter, the proportion of the latter usually increasing with the total amount of residue.

Next ignite the residue in the platinum dish, at as low a temperature as possible, until the carbonaceous matter is completely burnt. Cool and weigh the ash.

$$\text{Percentage ash} = \frac{\text{Weight of ash} \times 100}{\text{Weight of sample}}$$

$$\text{Percentage char} = \frac{(\text{Weight of carbonaceous residue} - \text{weight of ash residue}) \times 100}{\text{Weight of sample}}$$

It is difficult to avoid volatilising some of the NaCl present when heating to obtain the ash. But if the amount of NaCl does not exceed the usual specification limit of 0.01 per cent. (calculated as Cl), the error is negligible.

In cases, however, where much salt is present, it is best to extract the salts from a portion of the "*char*" by lixiviating with boiling water and filtering and then

recovering them by evaporation. The insoluble residue is then ignited and the weight of ash added to the weight of residue from the evaporation. This gives the total ash.

(3) **Chlorides.**—About 10 c.c. of hot distilled water are added to the ash residue in the platinum dish, and the mass is triturated with the end of a glass rod. The contents of dish are afterwards washed on to a filter, thoroughly washed with hot distilled water, and the filtrate is caught in a porcelain evaporating bowl.

Now add 1 c.c. of potassium chromate indicator and 1-2 mg. of  $\text{Na}_2\text{CO}_3$ . Titrate to the first permanent reddish tint with N/100  $\text{AgNO}_3$  solution.

Then 
$$1 \text{ c.c. of } \frac{\text{N}}{100} \text{ AgNO}_3 = 0.0003546 \text{ g. Cl,}$$

and 
$$\text{Percentage chlorides as Cl} = \frac{\text{No. c.c. } \frac{\text{N}}{100} \text{ AgNO}_3 \times 0.0003546 \times 100}{\text{Weight of sample}}.$$

This method of working is accurate enough for most purposes. More accurate results may be obtained by estimating the chlorine in the evaporated residue from the extracted "char," to which has been added the soluble portion of the ignited char. It should be noted that a direct titration of the chlorides made by merely diluting the glycerol always gives low results, because the brownish tint produced by the foreign matter present renders the end point of the titration with chromate as indicator very difficult to distinguish.

(4) **Silver Nitrate Test.**—Ten c.c. of a 10 per cent solution of silver nitrate are placed in a small glass-stoppered cylinder, 10 c.c. of the sample of glycerol is added, and the two liquids are thoroughly mixed by repeatedly inverting the cylinder.

Avoid vigorous agitation which would introduce air bubbles, and perform the whole operation as rapidly as possible in a subdued light.

Allow the cylinder to stand for ten minutes in a perfectly dark place and then inspect the appearance of the mixture by transmitted light in order to see whether any colour change or precipitate has been produced.

This test was devised for the detection of acrolein, formic acid, butyric acid, and similar organic substances which reduce silver nitrate. The test however, is now considered to be of little significance except when marked results are obtained.

(5) **Odour.**—The odour of the sample should be observed. So much depends upon the personal element that unless extreme results are observed, this test is of little value.

(6) **Suspended Matter.**—This is observed by viewing the sample placed in an ordinary test tube against a white surface.

This also is a test of little significance, except in extreme cases.

(7) **Glycerol Content by the Acetin Process.**—This is estimated in the same way as for *crude glycerol*, described on p. 9.

The acetin method accurately estimates the glycerol content in pure refined glycerol. It is, therefore, a valuable check on adulteration with impurities which leave the specific gravity of the sample unchanged.

(8) **Estimation of Moisture in Glycerol.**—The estimation of water in glycerol is important for some purposes, especially for calculating the percentage of trimethylene glycol present.

C. A. Rojahn (*Zeit. Anal. Chem.*, 1919, 58, 433) determines the moisture by drying 2 g. of the sample on asbestos under reduced pressure over phosphorus pentoxide in a desiccator. The drying should not be prolonged over forty-eight hours, as the glycol is slightly volatile.

*Lewis and Bond* (of the du Pont de Nemours Explosive Co., U.S.A.; see *Allan's "Commercial Analysis,"* 5th Edition, 1924, p. 721, where the method is given in detail) develop the method, placing about 1 g. of glycerol on glass wool in a tared bottle which is placed in a vacuum desiccator containing phosphorus pentoxide, allowing to stand twenty-four hours under a vacuum of 12-15 mm., and then estimating the loss of weight.

Since glycerol is very hygroscopic, great care must be taken in carrying out all the operations in such a way that moisture contained in the air does not get the opportunity of being absorbed by the glycerol.

Hence the bottle must be dried at 120° C. and be cooled in a vacuum desiccator; the glycerol must be rapidly introduced by means of a special pipette.

*I. M. Kolthoff* (*Pharm. Weekblad*, 1918, 55, 304-307) gives an account of a method of estimating the percentage of water in glycerine by observing the temperature range of complete miscibility of mixtures of the sample and aniline. A table showing the corresponding percentages of water is given.

## CHAPTER IX

## DISTILLED GLYCEROL—DETERMINATION OF TRIMETHYLENE GLYCOL THEREIN

## LITERATURE

A. H. SALWAY. *Jour. Soc. Chem. Ind.*, 1918, 37, 123 T., 158 T.

COCKS and SALWAY. *Jour. Soc. Chem. Ind.*, 1922, 41, 17 T.

C. A. ROJAHN. *Zeit. Anal. Chem.*, 1919, 58, 433.

FACHINI and SOMAZZI. *Chem. Trade Jour.*, 1923, 73, 127, 703.

**Determination of Trimethylene Glycol in Glycerol.**—The presence of trimethylene glycol in glycerol renders it unfit for the manufacture of explosives. Hence the determination of same is of importance.

Trimethylene glycol,  $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2\text{OH}$ , is considerably more volatile than glycerol,  $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$ , and has a much lower specific gravity than glycerol.

Thus pure trimethylene glycol has a specific gravity of 1.0554 at 20°/20° C. (against 1.2644 at 20°/20° C. for pure glycerol) and a boiling point of 210°-211° C. (against 290° C. for pure glycerol) at 760 mm. pressure and 171° C. at 174 mm. Consequently the presence of trimethylene glycol in glycerol is revealed by a low specific gravity, and the substance is found principally in the first fractions which distil.

A. H. Salway (*Jour. Soc. Chem. Ind.*, 1918, 123 T., 158 T.) estimates the amount of trimethylene glycol by determining the specific gravity and apparent glycerol content of the sample (by the acetin method).

If  $x$  and  $y$  are the percentages of *glycerol* and trimethylene glycol *by weight*, we have :—

$$\text{Specific gravity} = \frac{100}{100 - 0.2082x - 0.0503y} \quad . \quad . \quad (1)$$

$$\text{Apparent glycerol content} = x + 0.81y \quad . \quad . \quad (2)$$

From these two equations  $x$  and  $y$  can be calculated.

Unfortunately this method of calculation only gives approximate results, since it is based on the assumption that no contraction of volume occurs on mixing glycerol, trimethylene glycol, and water.

Cocks and Salway (*Jour. Soc. Chem. Ind.*, 1922, 41, 17 T.) increased the accuracy of the method by determining the specific gravity of a series of mixtures containing known quantities of glycerol, trimethylene glycol, and water, and from these results constructed tables from which the percentage of trimethylene glycol could be read off.

These solutions were obtained as follows :—

Six solutions of trimethylene glycol in standard 90 per cent. glycerol were made containing 2, 5, 10, 15, 20, and 25 per cent. respectively of trimethylene glycol.

Another series of six solutions of trimethylene glycol in water was made, also containing 2, 5, 10, 15, 20, and 25 per cent. of trimethylene glycol.

The 2 per cent. aqueous solution of trimethylene glycol was then added in successive amounts to the 2 per cent. solution in standard glycerol, and the specific gravity determined after each addition.

In this way a series of mixtures all containing 2 per cent. of trimethylene glycol, but varying amounts of glycerine and water, were obtained.

Similarly other series of mixtures were obtained, each series containing a constant trimethylene glycol content, but varying amounts of glycerol and water.

The following table was constructed from the results. In these tables the specific gravities and the *apparent glycerol contents* (acetin value) are given :—

TABLE II.—SPECIFIC GRAVITIES OF GLYCEROL SOLUTIONS CONTAINING VARIOUS PERCENTAGES OF TRIMETHYLENE GLYCOL. (COCKS AND SALWAY.)

Acetin Values of Solutions in Percentage of Glycerol.	Percentages of Trimethylene Glycol in the Solutions.						
	0	2	5	10	15	20	25
	Specific Gravities of Solutions at 20°/20° C.						
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
100	1.2644	...	...	...	...	...	...
99	1.2618	1.2577	1.2523	...	...	...	...
98	1.2591	1.2551	1.2497	1.2398	...	...	...
97	1.2565	1.2525	1.2472	1.2373	1.2287	...	...
96	1.2538	1.2499	1.2446	1.2348	1.2263	1.2175	...
95	1.2511	1.2473	1.2420	1.2323	1.2238	1.2151	1.2064
90	1.2378	1.2343	1.2291	1.2198	1.2115	1.2030	1.1944
85	1.2243	1.2211	1.2161	1.2073	1.1992	1.1909	1.1824
80	1.2108	1.2078	1.2032	1.1948	1.1868	1.1788	1.1704
75	1.1972	1.1943	1.1898	1.1818	1.1737	1.1659	1.1579
70	1.1836	1.1806	1.1763	1.1685	1.1606	1.1531	1.1454
65	1.1699	1.1670	1.1627	1.1550	1.1476	1.1402	1.1329
60	1.1563	1.1533	1.1490	1.1412	1.1346	1.1275	1.1204
55	1.1425	1.1396	1.1353	1.1275	1.1215	1.1147	1.1078
50	1.1288	1.1259	1.1216	1.1137	1.1084	1.1019	1.0952

From the tables it will be seen that the reduction in specific gravity with increasing trimethylene glycol content is nearly regular. For example, on examining the figures at a constant *acetin value*, say 75 per cent., we find that the change in *specific gravity* for each additional 5 per cent. trimethylene glycol is 0.0074, 0.0080, 0.0081, 0.0078, and 0.0080 respectively. Hence in order to calculate the *trimethylene glycol content* of any mixture :—

(1) Find from tables (see Section IV., Chapter I.) the specific gravity  $x$  of an aqueous glycerol solution at a dilution represented by the *acetin value* of the solution which is being examined.

(2) Subtract from  $x$  the specific gravity  $y$  of the solution which is being examined. We thus see the difference  $x - y$ .

(3) Divide the difference  $x - y$  by a certain factor  $A$  (which is deduced from the tables).

The result is the percentage  $P$  of trimethylene glycol :—

$$P = \frac{x - y}{A}$$

The factor  $A$  increases with the *acetin value* as follows :—

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TABLE III

Acetin Figure.	Factor A.	Acetin Figure.	Factor A.
Per Cent.		Per Cent.	
50	0.00134	75	0.00157
55	0.00138	80	0.00162
60	0.00143	85	0.00168
65	0.00148	90	0.00174
70	0.00152	95	0.00179

*Example.*—A given solution gave an acetin value of 67.8 and possessed a specific gravity of 1.1613 at 20°/20°. What is its trimethylene glycol content?

(1) By ordinary interpolation from Column 2 from Cocks and Salway's table above, we find that a pure aqueous solution of glycerol (*i.e.*, one containing 0 per cent. of trimethylene glycol) should possess the specific gravity at 20°/20° of :—

$$1.1699 + (67.8 - 65) \frac{(1.1836 - 1.1699)}{5} = 1.1776.$$

(2) The difference between the specific gravity and that of the solution to be tested for trimethylene glycol is  $1.1776 - 1.1613 = 0.0163$ .

(3) The factor corresponding to an acetin value of 67.8 is obtained by ordinary interpolation from Table III. above as :—

$$0.00148 + (67.8 - 65) \frac{(0.00152 - 0.00148)}{5} = 0.00150.$$

(4) Hence the required percentage of trimethylene glycol is :—

$$\frac{\text{Difference in expected and found specific gravity}}{\text{Factor}} = \frac{0.0163}{0.00150} = 11.0 \text{ per cent.}$$

**Cocks and Salway's Method for the Estimation of Trimethylene Glycol in Crude Glycerine** (*loc. cit.*, p. 19 T.).—"A known weight (100 g.) of the crude glycerine is introduced into a 600 c.c. distillation flask, which is fitted with a cork and capillary inlet tube. To the distilling flask is fitted an air condenser about 2 ft. 6 in. or 3 ft. long, and a receiver to collect the distillate. The apparatus is then evacuated (15-30 mm.) and the distillation commenced. For heating the glycerine, an oil bath at 230°-240° may be used, but occasionally trouble arises due to frothing. It is preferable to use a carefully manipulated smoky flame, by which means the frothing can be kept under better control. The heating should be so regulated that the distillation proceeds at about 1 drop per second and the distillation continued until approximately 30 per cent. of the weight of the original crude glycerine has collected in the receiver. In the early stages of the distillation the material loses its water, some of which escapes condensation. This is an advantage, as it obviates the necessity for concentrating the distillate before analysis.

"If any priming has occurred during the distillation, the distillate must be redistilled before analysis. For analysis the specific gravity and acetin value of the distillate are determined and the trimethylene glycol may then be read off from large scale curves constructed for the purpose, or may be calculated as recorded previously from the difference between the expected specific gravity and the gravity found."

## Other Methods of Estimating Trimethylene Glycol in Glycerol.

C. A. Rojahn (*Zeit. Anal. Chem.*, 1919, 58, 433) shows that the specific gravity of glycerine (1.2653 at 15°/15° C.) is lowered by the presence of trimethylene glycol (sp. gr. 1.0573) or water, or both. If the water content is known the amount of

the glycol present may be calculated from the specific gravity. The water is determined by drying 2 g. of the sample on asbestos under reduced pressure over phosphorus pentoxide; the drying should not be prolonged for more than forty-eight hours, as the glycol is slightly volatile. Graphs and tables are given showing the percentages of the glycol present in glycerine samples of varying specific gravity and water content.

*Fachini and Somazzi (B. d. Ind. d. Olii e dei Grassi, October 1923; Chem. Trade Jour. and Chem. Eng., 1923, 73, 127, 703)* work out a method based on the oxidation of the glycerol by dichromate solution, and this method appears to furnish correct results.

*Henkel und Co. (Seifenfabr., 1916, 36, 769-770; Zeit. Angew. Chem., 1917, 30, Ref. 108)* point out that crude glycerine made from waste fatty materials which have undergone some decomposition by fermentation may show abnormalities on analysis. Its specific gravity may be lower than usual and its oxidation value by the bichromate method may exceed 100 per cent. This has been traced to the presence of n-propylene glycol (trimethylene glycol). It is stated that the quantitative determination of glycerol in presence of the latter can be made by the isopropyl iodide method of *Zeisel and Stritar (Jour. Soc. Chem. Ind., 1902, 992)*.

However, *C. A. Rojahn (Ber., 1919, 52, 1454-1460)* shows that *Zeisel's* method (*Jour. Soc. Chem. Ind., 1902, 992*) is not applicable to the estimation of fermentation glycerol (the German "protol" glycerol), for this contains trimethylene glycol, which develops di-isopropene. This passes over more or less completely with the isopropyl iodide, although its boiling point is much above the reaction temperature (120°-125° C.).





## INDEX OF AUTHORITIES

**Directions for Using Index.**—The *Volume Number* comes *first*; the *Section Number* comes *second*; the *Section Page* comes *third*.

*Example.*—*Acheson*, 2.7.10, means that a reference to Acheson occurs in *Volume 2*, *Section 7*, *Page 10*.

*Note that :—*

The *Volume Number* occurs at bottom of page, in the *Left-hand Corner*.

The *Section Number* occurs at bottom of page, in the *Right-hand Corner*.

The *Page Numbers* occur at top of pages, in the usual position.



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*Example.*—*Abrasive Soaps*, 2.4.38-46, means that the subject of abrasive soaps is discussed in *Volume 2*, *Section 4*, and *Pages 38-46* of *Section 4*.

*Note that :—*

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